Rocky Mountain Conference on Magnetic Resonance

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August 1983

25th Rocky Mountain Conference

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ABSTRACTS & MEETING PROGRAM

Sponsored jointly by

Rocky Mountain Section
Society for Applied
Spectroscopy

and

Rocky Mountain Chromatography Discussion Group

DENVER CONVENTION COMPLEX

Denver, Colorado

August 14–17, 1983

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1983

WELCOME

For the past 24 years, the Denver area has hosted the Rocky Mountain Conference. From a modest beginning as a local meeting on applied spectroscopy, the Conference has evolved into an exciting, international meeting encompassing the major concerns of today's analytical chemists.

In this our 25th year, I welcome and thank all of the individuals who have contributed to this success. I wish to convey special thanks to those who have donated their time and materials to make this "Silver Anniversary" conference possible.

This year more than 300 papers and posters are to be presented in the twelve symposia. In addition, a variety of exhibits and social activities are scheduled for your information and entertainment.

For those of you visiting us from out-of-state, I hope you will enjoy your stay and plan to observe some of this area's special features that make those of us living here justifiably proud of Denver and Colorado.

Sincerely,

Edward A. Brovsky

Edward A. Brovsky
Conference Chairman

REGISTRATION HOURS AND LOCATION

Sunday,	August 14,	Executive Tower Inn	4:00 p.m. - 8:00 p.m.
Monday,	August 15,	Denver Convention Complex	7:30 a.m. - 3:30 p.m.
Tuesday,	August 16,	Denver Convention Complex	7:30 a.m. - 3:30 p.m.
Wednesday,	August 17,	Denver Convention Complex	7:30 a.m. - 3:30 p.m.

REGISTRATION FEES

Preregistration	$30.00
Registration at Conference	$35.00
Registration one day only	$20.00
Students	$10.00
Unemployed or retired	No charge

Badges are required for admission to all technical programs and to the exhibit area. "Exhibit Area Only" badges can be obtained at the registration desk for those not wishing to attend technical meetings. No Charge.

VISITOR INFORMATION

Information on the Denver area may be obtained from the Denver Convention and Visitors Bureau, 225 West Colfax Avenue, Denver, CO 80202 (Phone 303/892-1112).

SOCIAL FUNCTIONS

MIXER

All conference attendees and spouses are invited to a mixer on Monday, August 15, from 5:30 p.m. to 8:00 p.m. at the Executive Tower Inn.

CONFERENCE BANQUET

The Conference Banquet will be held on Tuesday, August 16, at 7:00 p.m. at the Executive Tower Inn. Tickets are $14.00 each. There will be a cash bar in the banquet area at 6:30 p.m.

This year our banquet program is presented by Major Ronald J. Grabe, USAF, an informed and entertaining speaker from NASA (Lyndon B. Johnson Space Center). Major Grabe, an astronaut with the Space Center, will be speaking on the current and future activities in space.

DINNER - THEATER

The conference has arranged for a limited number of tickets to the Wednesday, August 17, evening performance of "MUSIC MAN" at the Boulder Dinner Theater. An "order from the menu" dinner is served prior to the performance. Tickets for the dinner and show (including tax and tip) are $16.00 each. Buses have been reserved for those requiring transportation. Cost is $6.00 per person. The dinner theater tickets and transportation (if required) may be purchased at the registration desk while they last. Dinner will be served at 6:15, and buses will leave from the Executive Tower Inn at 5:15.

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TOURS

Tour 1: Tuesday, August 16 - A 7-hour Gray Line bus tour to visit the Colorado Air Force Academy and the Garden of the Gods is offered to attendees' spouses and families. Stops at the Broadmoor Hotel Resort, Manitou Springs, and the Van Briggle Potters are also planned. You will be given time to enjoy the spectacular sights of red sandstone sculptures, and the impressive architecture at the Air Force Academy. Cost for this tour is $15.00, meals not included.

Tour 2: Thursday August 18 - A 10-hour "Colorado Mountain Tour" has been arranged through Gray Line Tours. The trip goes through Clear Creek Canyon, over the Continental Divide to Winter Park Ski Area, and on to picturesque Grand Lake for lunch. The afternoon will be spent touring Rocky Mountain National Park, including a drive over Trail Ridge Road (the highest continuous automobile road in North America). The return to Denver will be via Estes Park and through the beautiful Big Thompson Canyon. Cost for this tour is $25.00, meals not included.

FILM FESTIVAL

The following films will be shown at various times on Monday, Tuesday, and Wednesday of the Conference:

KEYHOLE OF ETERNITY, 27 minutes, color, 1975.
WEATHER: WHO VOTES FOR RAIN?, 23 minutes, color, 1973.
VISIONS OF TOMORROW, 28 minutes, color, 1977.
GEOTHERMAL: THE ENERGY WITHIN, 17 minutes, color, 1980.
ENERGY SEEKERS, 12 minutes, color, 1980.
ROBOTICS: ISAAC ASIMOV'S (CLANK!CLANK!) ARTIFICIAL MAN, 23 minutes, color, 1972.
THE LIMITS TO GROWTH, 55 minutes, color, 1973.
NOBODY'S PERFECT, 24 minutes, color, 1980.
LIVING WATERS OF THE COLORADO, 22 minutes, color, 1981.
ACID FROM HEAVEN
ACID RAIN - REQUIEM OR RECOVERY

The films may be viewed by conference attendees and families without charge. Family members may obtain a badge for admission to the films at the registration desk.

EMPLOYMENT CLEARING HOUSE

An employment clearing house booth will be in operation during regular conference hours. This service will be available to all conferees. Location of the booth will be posted at the registration desk. Bulletion board space will be provided in the booth for employers to post job announcements. There will also be a notebook provided for conferees to post resumes. A list of Denver Metropolitan area employers will be available upon request. The conference (employment clearing house) will not assume obligation for the qualifications of job candidates, confidentiality of information exchanged, or the responsibility of employers.

MESSAGE CENTER

A message center has been set up for Conference attendees in the registration area. The number is (303) 623-3440. The message center will be open from 8:00 a.m. to 4:30 p.m.(MDT) on Monday, Tuesday, and Wednesday. This service is for incoming calls only.

There are numerous pay phones in the Convention complex for outgoing calls.

Future Conference Dates

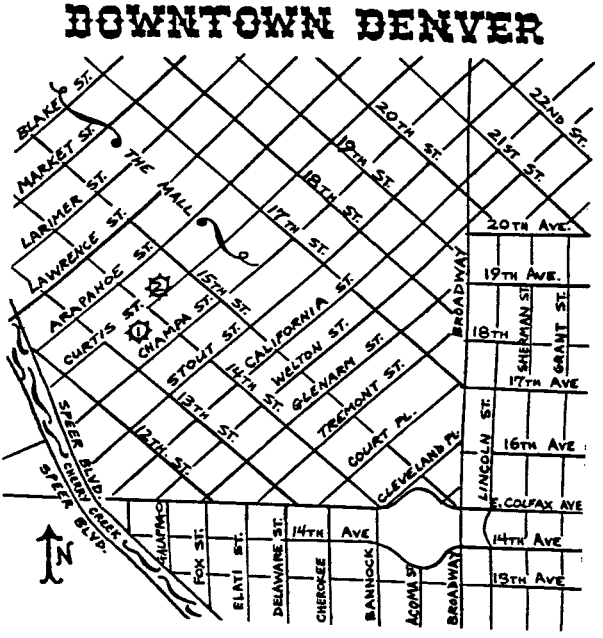
August 5 - 10, 1984

July 14 - 19, 1985

August 3 - 8, 1986

July 26 - 31, 1987

July 30 - August 5, 1988



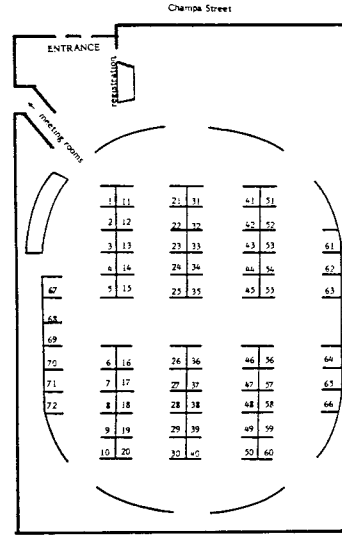
1. CONVENTION COMPLEX
2. EXECUTIVE TOWER INN

CONFERENCE EXHIBITION

Exhibits of new chemical products, instruments, and services will be on display in the Denver Convention Complex. Exhibit hours will be 10:00 a.m. - 5:00 p.m. on Monday, 9:00 a.m. - 5:00 p.m. on Tuesday , and 9:00 a.m. to 3:00 p.m. on Wednesday. The exhibits are an important part of the Conference, so set aside time in your schedule to visit them and learn what's new in laboratory apparatus. The sponsoring societies of the Conference gratefully acknowledge the exhibitors support.

C O N F E R E N C E E X H I B I T O R S
(as of May 26)

	Booth No.
ACE Glass, Inc.	24
Air-Row Instruments	18-19
Allen Scientific Glass Blowers, Inc.	5
Alltech/Applied Science	35
American Scientific Products	17
Beckman Instruments	67-69
Bio-Rad Laboratories	43
Brinkmann Instruments	10
Certified Balance Service, Inc.	8
Colorado Analytical Group	34
Coulometrics, Inc.	45
Digilab	42
Digital Equipment Co.	66
Dionex	2-3
ECO Instruments	20
EM Science/MCB Reagents	25
Finnigan-MAT	46
Gow-Mac Instrument Co.	55
Hach Co.	16
Harris Analytical	28-30,38-40
Hauser Laboratories	7
Hewlett-Packard Co.	14-15
IBM Instruments	62-63
Instrumentation Laboratories, Inc.	49-50
LDC/Milton Roy	56-57
LKB Instruments	13
Luxtron Corp.	37
Masscomp	70
Nicolet Analytical Instruments	26
Nicolet Magnetics Corp.	27
Perkin-Elmer Corp.	21-23,31-33
Rocky Mountain Analytical Laboratories	12
Sadtler Research Laboratories	41
Sargent-Welch Scientific Co.	64-65
Scientific Glass Engineering, Inc.	4
SCT Sales	1-11
Torrtek Industries, Inc.	47-48
Wescan Instruments, Inc.	6
Whatman, Inc.	44
Wilmad Glass Co., Inc.	51
Varian Instruments	36



ORGANIZERS OF THE 25TH ROCKY MOUNTAIN CONFERENCE

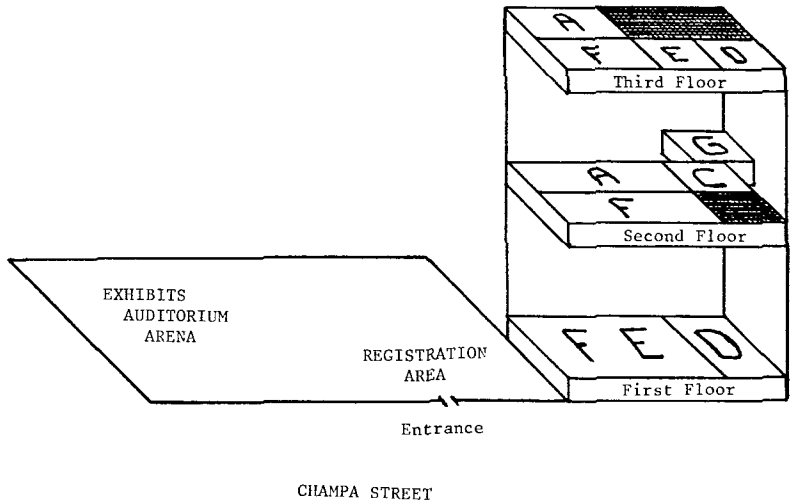
Conference Chairperson	E. A. Brovsky Rockwell International
Conference Vice Chairperson Registration/Treasurer	J. L. Gurnsey
Exhibits/Facility	K. Brooks University of Colorado
	J. Otto Cord Laboratories
Printing	J. D. Grooms Rockwell International
Publicity	M. Brooks U. S. Geological Survey
Banquet/Mixer	L. Lockrem Reservoirs Inc.
Visitor Information	G. Brown Rockwell International
Audio-Visual	D. Raines Huffman Laboratories
Employment	H. Miller U. S. Geological Survey

SYMPOSIA CHAIRPERSONS

Atomic Spectroscopy	T. Niemczyk University of New Mexico
Chromatography	R. Barkley University of Colorado
Computer Applications	F. Settle Virginia Military Institute
Electrochemistry	C. A. Koval University of Colorado C. M. Elliott Colorado State University
Environmental	M. M. Reddy U. S. Geological Survey
EPR Spectroscopy	G. R. Eaton S. S. Eaton University of Denver
FTIR Spectroscopy	D. Smith University of Denver
Ion Chromatography	M. J. Fishman U. S. Geological Survey
Mass Spectroscopy	M. Bergeron Rockwell International
NMR Spectroscopy	F. Miknis Laramie Energy Technology Center
Raman Spectroscopy	M. Goldberg U. S. Geological Survey
Surface Analysis	B. Phillips Perkin-Elmer
Poster Session	C. Arozarena U. S. Geological Survey

TECHNICAL PROGRAM

	Floor	Rm	MORNING	Floor	Rm	AFTERNOON
Monday	2nd	G	EPR Session I	2nd	G	EPR Session II
August 15	2nd	C	NMR Session I	2nd	C	NMR Session II
	2nd	A	Ion Chromatography	2nd	A	Ion Chromatography
	3rd	F	FTIR Spectroscopy	3rd	E	Environmental
	3rd	D	Electrochemistry	3rd	D	Electrochemistry
	2nd	F	Computer Applications	2nd	F	Computer Applications
	3rd	E	Raman Spectroscopy	3rd	F	IR Spectroscopy
	3rd	A	Chromatography	3rd	A	Chromatography
	1st	F	General Posters	1st	F	General Posters
Tuesday	2nd	G	EPR Session III	2nd	G	EPR Session IV & V
August 16	2nd	C	NMR Session III	1st	F	EPR Session V (Posters)
	2nd	A	Ion Chromatography	2nd	C	NMR Session IV
	3rd	E	Environmental	1st	F	NMR Poster Session
	3rd	D	Electrochemistry	2nd	A	Ion Chromatography
	3rd	A	Surface Analysis	3rd	E	Environmental
	3rd	F	FTIR Spectroscopy	3rd	D	Electrochemistry
	2nd	F	Atomic Spectroscopy	3rd	A	Surface Analysis
				3rd	F	IR Spectroscopy
				2nd	F	Atomic Spectroscopy
Wednesday	2nd	G	EPR Sessions VI	2nd	G	EPR Session VIII
August 17	1st	F	EPR Session VII (Posters)	2nd	C	NMR Session VI
	2nd	C	NMR Session V	2nd	A	Ion Chromatography
	2nd	A	Ion Chromatography	3rd	F	FTIR Spectroscopy
	3rd	F	FTIR Spectroscopy	2nd	F	Atomic Spectroscopy
	2nd	F	Atomic Spectroscopy			
	3rd	E	Environmental			
	3rd	D	Mass Spectroscopy			
	3rd	A	General Session			



SYMPOSIUM ON CHROMATOGRAPHY

MONDAY MORNING, AUGUST 15, 1983 - Third Floor, Room A
R. M. Barkley, Presiding

8:30 28. "Identification of Insoluble Organic Particulate Material from Vehicular Traffic," K. J. Voorhees and W. D. Schulz, Colorado School of Mines, Golden, Colorado.

8:50 29. "Development of Chromatographic Techniques for the Analysis of Synfuel Samples," A. P. Toste, T. R. Pahl and R. B. Myers, Pacific Northwest Laboratory, Richland, Washington

9:10 30. "Determination of Selenium in Marine Sediments by Gas Chromatography," K. W. M. Siu and S. S. Berman, National Research Council of Canada, Ottawa, Ontario

9:30 31. "Application of Capillary Gas Chromatography to the Analysis of Pesticide and Industrial Chemical Residues in Foods," N. V. Fehringer and S. M. Walters, U. S. Food and Drug Administration, Detroit, Michigan

9:50 32. "Energy Transfer Chemiluminescence Detection of Polycyclic Aromatic Amines in HPLC," K. W. Sigvardson and J. W. Birks, University of Colorado, Boulder, Colorado

10:10 Break

10:20 33. Plenary Lecture - "The Renaissance in Analytical Chromatography," W. Jennings, University of California, Davis, California

11:20 34. "Selective Sorption of Aldehydes, Ketones and Alcohols Based on Complexation," E. J. Williams and R. E. Sievers, University of Colorado, Boulder, Colorado

11:40 35. "Simultaneous Quantitative Analysis Using Dual Capillary Columns of Different Polarities," C. Wright, Pacific Northwest Laboratory, Richland, Washington

SYMPOSIUM ON COMPUTER APPLICATIONS

MONDAY MORNING, AUGUST 15, 1983 - Second Floor, Room F

8:30 45. Invited Speaker - "Future Applications of Computers in R&D," K. J. Caserta, The Proctor & Gamble Company, Cincinnati, Ohio

9:20 46. Invited Speaker - "Languages, Operating Systems and Networks," R. E. Dessy, Virginia Polytechnic Institute and State University, Blacksburg, Virginia

10:10 47. "A Microcomputer Network for the Small Industrial-Clinical-Analytical Laboratory," J. J. Brosemer and D. J. Macero, Syracuse University, Syracuse, New York

10:30 Break

10:40 48. Invited Speaker - "The Use of Color Graphics as an Analytical Tool in the Analytical Laboratory," P. V. Passalacqua, Perkin - Elmer Corp., Norwalk, Connecticut

11:10 49. "Computer Modeling of Chromatographic Curves Produced by an On-Column Reaction," A. J. Boyer and T. W. Gilbert, University of Cincinnati, Cincinnati, Ohio

11:30 50. "A Microcomputer Controlled Automatic Titration System," A. L. Lewis and D. R. Trammell, Exxon Nuclear Idaho Co., Inc., Idaho Falls, Idaho

SYMPOSIUM ON ELECTROCHEMISTRY

MONDAY MORNING, AUGUST 15, 1983 - Third Floor, Room D
Session on Polymer-coated Electrodes - C. A. Koval, Presiding

9:00 58. "Spatially and Chemically Modified Electrodes," R. W. Murray, P. Burgmayer, P. Pickup, and C. R. Leidner, University of North Carolina, Chapel Hill, North Carolina

10:00 59. "Surface-modified CdS Photochemical Diodes: Water-cleavage Reaction," K. Honda and A. J. Frank, Solar Energy Research Institute, Golden, Colorado

10:45 60. "Modification of Electrode Surfaces with Polymer Bound Transition Metal Phosphine Complexes," D. L. Dubois, Photoconversion Research Branch, Solar Energy Research Institute, Golden, Colorado

11:30 61. "Electrochemical (and other) Investigations of the Ion-Exchange Selectivities and Transport Properties of Various Ion-containing Polymers," J. A. Ferguson, M. N. Szentirmay, N. E. Prieto, and C. R. Martin, Texas A & M University

6TH INTERNATIONAL ELECTRON PARAMAGNETIC RESONANCE SYMPOSIUM

MONDAY MORNING, AUGUST 15, 1983 - Second Floor, Room G
EPR SESSION I - G. R. Eaton, Presiding

8:50 Introductory Remarks - G. R. Eaton

9:00 104. Plenary Lecture - "Electron-Nuclear Multiple Resonance in Photochemistry: Hyperfine Structure of Short-Lived Radicals," K. Möbius, Free University, Berlin

10:00 105. "A Time-Resolved EPR Study of the Non-Phosphorescent Triplet States: Ortho Diazaaromatics," S. Yamauchi, M. Terazima, and N. Hirota, Kyoto University

10:20 Break

10:50 106. "The Interpretation of Spin-Polarized (CIDEP) Spectra," K. A. McLauchlan, Oxford University

11:40 107. "Electron Spin-Echo Characterization of Collisions Between Reactive Radicals in Solution," D. M. Bartels, A. D. Trifunac, and R. G. Lawler, Argonne National Laboratory and Brown University

SYMPOSIUM ON FOURIER TRANSFORM INFRARED SPECTROSCOPY AND ITS APPLICATION

MONDAY MORNING, AUGUST 15, 1983 - Third Floor, Room F
FTIR SESSION I - D. M. Smith, Presiding

8:55 Introductory Remarks, D. M. Smith

9:00 157. Plenary Lecture - "Chemistry and Structure of Coals: Diffuse Reflectance Infrared Fourier Transform Spectroscopy of Surface Reactions," E. L. Fuller, Jr. and N. R. Smyrl, Oak Ridge Y-12 Plant, Union Carbide Corporation, Oak Ridge, Tennessee

9:50 158. "The Characterization of Soot by FTIR and Other Techniques," M. S. Akhter, A. R. Chughtai, and D. M. Smith, University of Denver, Denver, Colorado

10:10 159. "Kinetics of the Reaction of NO_2 with Soot," M. S. Akhter, A. R. Chughtai, and D. M. Smith, University of Denver, Denver, Colorado

10:30 Break

10:50 160. "FT-IR Studies of the Gas Phase Reactions of Ozone with Hydrazine and Methyl-Substituted Hydrazines," E. C. Tuazon, W. P. L. Carter, A. M. Winer, R. Atkinson, and J. N. Pitts, Jr., University of California, Riverside, California

11:15 161. "Applications of FTIR and Reaction Modeling to Problems of Instability of NO in N_2 Gas Mixtures," B. C. Cadoff, National Bureau of Standards, Washington, D. C.

11:40 162. "In Situ Measurement of Combustion Gases Using Fourier Transform Infrared (FTIR) Spectrometry," L. R. Thorne and D. K. Ottesen, Sandia National Laboratories, Livermore, California

GENERAL SESSION - POSTERS

MONDAY AUGUST 15 - First Floor, Rooms E - F
C. Arozarena, Presiding

Posters displayed all day - Authors present 2:00 - 4:00

(See Monday afternoon for paper titles)

SYMPOSIUM ON ION CHROMATOGRAPHY

MONDAY MORNING, AUGUST 15, 1983 - Second Floor, Room A
A. G. Hedley, Presiding

8:30 Introductory Remarks - A. G. Hedley

8:35 211. Keynote Speaker - "Single-Column Ion Chromatography," J. E. Girard, The American University, Washington, D. C.

9:20 212. "A Sequential Method of Analysis for Fluoride and Chloride by Ion Chromatography," J. J. Rios and V. C. Anselmo, Texas Air Control Board, Austin, Texas

9:45 Break

10:15 213. "Ion Chromatographic Analysis of Indoor and Outdoor Aerosol Particles Collected on Teflon Filters," S. P. Kelty, L. A. Psota-Kelty, J. D. Sinclair, and C. J. Weschler, Bell Laboratories, Holmdel, New Jersey

10:35 214. "Accumulation Rates of Ionic Substances on Indoor Surfaces," G. B. Munier, L. A. Psota-Kelty, and J. D. Sinclair, Bell Laboratories, Holmdel, New Jersey

11:00 215. "New Developments in Ion Chromatography," C. A. Pohl, M. E. Ebenhahn, S. Papanu, G. Hennion, and A. Woodruff, Dionex Corp., Sunnyvale, California

11:25 216. "Anion Separations by Ion Chromatography Using Dilute Eluents," R. E. Truitt, Celanese Research Company, Summit, New Jersey

SYMPOSIUM ON NUCLEAR MAGNETIC RESONANCE

MONDAY MORNING, AUGUST 15, 1983 - Second Floor, Room C
NMR SESSION I

8:50 Introductory Remarks - F. P. Miknis

9:00 252. Robert Vaughan Plenary Lecture - "High Resolution NMR of Aluminosilicates," E. Lippmaa, Estonian Academy of Sciences, Tallinn, Estonia, USSR

10:00 253. "Moment Analysis of ^{29}Si NMR Spectra for Characterization of Short Range Si/Al Ordering in Zeolites," A. J. Vega, E. I. du Pont de Nemours & Company, Wilmington, Delaware

10:30 Break

11:00 254. "^{29}Si and ^{27}Al High Field MAS NMR Structural Studies of Zeolite Catalysts," C. A. Fyfe, G. C. Gobbi, and G. J. Kennedy, University of Guelph, Guelph, Ontario, Canada, and (in part R. O-Uzko and W. J. Murphy), Imperial Oil, Ltd., Sarnia, Ontario, Canada

11:30 255. "A Comparative Study of the Properties of Offretite and ZSM-34," B. C. Gerstein and T. M. Apple, Iowa State University, Ames, Iowa. R. A. Innes and M. L. Occelli, Gulf Research and Development Company, Pittsburgh, Pennsylvania

SYMPOSIUM ON RAMAN SPECTROSCOPY

MONDAY MORNING, AUGUST 15, 1983 - Third Floor, Room E
RAMAN SPECTROSCOPY - J. E. Griffiths, Presiding

8:45 Introduction - J. E. Griffiths

9:00 288. "Raman Investigation of Aqueous Zinc Bromide Complexes," C. A. Cody, B. K. Faulseit, and W. W. Reichert, NL Chemicals. R. K. Darlington, NL Baroid

9:30 289. "The Use of Raman and MicroRaman Techniques in the Study of Kevlar 49 Degradation," F. P. Milanovich, S. Miller, T. Hirschfeld, and S. M. Klainer, ST&E Technical Services, Inc.

10:00 Break

10:30 290. "Raman Spectra of Microsamples Obtained with an Intensified Diode Array Spectrograph," D. O. Landon and D. G. Jones, Tracor Northern Inc. E. S. Etz, National Bureau of Standards

11:00 291. "Low Frequency Dye Laser Raman Spectroscopy," J. E. Griffiths, Bell Laboratories

11:30 292. "Trace Analysis of Moisture in Integrated Circuit Packages Using Derivative Diode Laser Spectroscopy," J. A. Mucha, Bell Laboratories

SYMPOSIUM ON CHROMATOGRAPHY

MONDAY AFTERNOON, AUGUST 15, 1983 - Third Floor, Room A
R. M. Barkley, Presiding

1:30 36. "NMR Studies of Chromatographic Surfaces," R. K. Gilpin, IBM Instruments, Inc., Danbury, Connecticut

1:50 37. "HPLC of Noble-Metal-8-Hydroxyquinolinates," B. Wenclawiak and F. Bickmann, WWU Anorg. Chem. Inst., Münster, W. Germany

2:10 38. "High Performance Liquid Chromatographic Measurement of Nitrite in Aqueous Solution by In Situ Formation of Methyl Nitrite," N. E. Skelly, A. C. Oomens and F. G. Schuurhuis, The Dow Chemical Co., Midland, Michigan

2:30 39. "The Estimation of Physico-Chemical Properties by GC/LC Techniques," R. C. Crippen, Crippen Laboratories, Inc., New Castle, Delaware

2:50 40. "Fluorocarbon Polymer Derivatives as HPLC Packings," R. W. Siergiej and N. D. Danielson, Miami University, Oxford, Ohio

3:10 Break

3:35 41. "Dating of Nineteenth Century Navajo Textiles via the HPLC Identification of Red Pigments," A. L. Hedlund, J. B. Wheat, R. E. Sievers and K. C. Brooks, University of Colorado, Boulder, Colorado

3:55 42. "Deconvolution of Multicomponent Liquid Chromatographic Peaks Using Complete Excitation - Emission Fluorescence Spectra," D. E. Seizinger, U. S. Department of Energy, Bartlesville, Oklahoma

4:15 43. "Applications for Chromatography in the Semiconductor Industry," J. A. Fulton and H. M. Gordon, Western Electric Co., Princeton, New Jersey

4:55 44. "Preparation of a Primary Natural Gas Standard for Calorific and Specific Gravity Calculation from Gas Chromatograph Analysis," R. E. Stern, Colorado Interstate Co., Pueblo, Colorado

SYMPOSIUM ON COMPUTER APPLICATIONS

MONDAY AFTERNOON, AUGUST 15, 1983 - Second Floor, Room F

1:30 51. Invited Speaker - "The Interaction of Networking, Sample Information Management and Chromatographic Analysis," D. Beggs, D. Greig, J. Justice, and E. Long, Nelson Analytical, Inc., Cupertino, California

2:00 52. "Transform Data Processing Techniques Applied to Cross-Correlation Chromatography," S. R. Frazer and M. F. Burke, University of Arizona, Tucson, Arizona

2:20 53. "Processing Chromatographic Data Using a Personal Computer," D. Klopp, Hewlett-Packard Co., Avondale, Pennsylvania

2:40 54. "A Microprocessor-Based Data System for Continuous Flow Analyzers," C. B. Ranger, Lachat Instrument Division, Mequon, Wisconsin

3:00 55. "Computer Applications in Petroleum Resource Appraisal," R. A. Crovelli, U. S. Geological Survey, Denver, Colorado

3:20 Break

3:30 56. "Microcomputer-Based Electronic Handbook of Chemical Instrumentation," F. A. Settle, Jr. and M. A. Pleva, Virginia Military Institute, Washington and Lee University, Lexington, Virginia

3:50 57. "Utilization of a Data Base Management System in the Undergraduate Instrumental Methods of Analysis Laboratory," R. J. Merrer, Western Connecticut University, Danbury, Connecticut

SYMPOSIUM ON ELECTROCHEMISTRY

MONDAY AFTERNOON, AUGUST 15, 1983 - Third Floor, Room D
Session on Polymer-coated Electrodes - C. A. Koval, Presiding

1:30 62. "Electron Shuttling by Added Redox Couples to Enhance Electrocatalytic Rates at Electrodes Coated with Nafion Films," D. A. Buttry and F. C. Anson, California Institute of Technology, Pasadena, California

2:15 63. "Thick-Nafion-Film Modified Electrodes," C. M. Elliott and J. G. Redepenning, Colorado State University, Fort Collins, Colorado

3:00 Break

3:30 64. "Luminescence Probe of Polymer Morphology in Thin Electrode Films," M. Majda, University of California, Berkeley, California

4:15 65. "Electochemistry and ESR of Tetracyanoquinodimethane Modified Electrodes," J. Q. Chambers, G. Inzelt, and R. W. Day, University of Tennessee, Knoxville, Tennessee

SYMPOSIUM ON ENVIRONMENTAL CHEMISTRY

MONDAY AFTERNOON, AUGUST 15, 1983 - Third Floor, Room E
M. M. Reddy, Presiding

2:00 Introduction and welcome - M. M. Reddy

2:10 75. "Advances in Ion Chromatography in the Area of Environmental Sciences," A. W. Fitchett, Dionex Corporation, Sunnyvale, California

2:40 76. "New Developments in NBS Environmental and Biological Standard Reference Materials Certified for Trace Constituents," R. Alvarez, Office of Standard Reference Materials, National Bureau of Standards, Washington, DC

3:00 77. "Silver in the Marine Environment: A Preliminary Budget for Puget Sound," N. S. Bloom and E. C. Crecelius, Battelle Marine Research Laboratory, Sequim, Washington

3:20 Break

3:40 78. "Accidental and Incidental Honeybee Poisoning by Pesticides," T. D. Spittler, J. B. Bourke, and R. A. Morse, New York State Agricultural Experiment Station, Cornell University, Geneva, New York

4:00 79. "The Development of a Conceptual Landscape Model to Assess the Effects of Acidic Deposition on Drinking Water Supplies," J. C. Meranger and T. H. Kahn, National Health and Welfare, Ottawa, Ontario, Canada. D. Gladwell, R. Lett, and C. Succi(Vairo), Barringer Magenta Ltd., Rexdale, Ontario, Canada

6TH INTERNATIONAL ELECTRON PARAMAGNETIC RESONANCE SYMPOSIUM

MONDAY AFTERNOON, AUGUST 15, 1983 - Second Floor, Room G
EPR SESSION II - W. E. Antholine, Presiding

2:00 108. Plenary Lecture - "Identification and Characterization of the Primary Reactant in Bacterial Photosynthesis by EPR," G. Feher, University of California, San Diego

2:50 109. "EPR and ENDOR Characteristics of Signals I and II in Spinach Chloroplasts," P. J. O'Malley and G. T. Babcock, Michigan State University

3:10 Break

3:40 110. "Magnetic Measurements of Thulium Nicotinate Dihydrate," C. A. Hutchison, Jr., J. M. Baker, B. Bleaney, J. S. Brown, M. J. M. Leask, P. M. Martineau, and M. R. Wells, Chicago University and Oxford University

4:30 111. "EPR Studies on Pairs of Jahn-Teller Distorted Hexakis Pyridine-N-Oxide Copper (II), $Cu(C_5H_5NO)_6^{2+}$ Ions," E. de Boer, C. P. Keijzers, G. van Kalkeren, and J. S. Wood, University of Nijmegen

GENERAL SESSION - POSTERS

MONDAY AUGUST 15 - First Floor, Rooms E - F
C. Arozarena, Presiding

Posters displayed all day - Authors present 2:00 - 4:00

181. "A Rapid Method for Determination of Nitrosoamine Formed from Rhodamine Dye and Nitrite Ion in River Water," S. M. Johnson and T. R. Steinheimer, U. S. Geological Survey

182. "Fluorescence Spectroscopy Applied to the Interpretation of Fulvic Acid Bonding to Copper in Aqueous Systems," M. C. Goldberg, U. S. Geological Survey

183. "Photolysis of Diols in Aqueous Systems," K. M. Cunningham and M. C. Goldberg, U. S. Geological Survey

184. "Review of Light Scattering Techniques for Particle Size and Mass Measurements in Aqueous Systems," M. C. Goldberg, K. M. Cunningham, and E. R. Weiner, U. S. Geological Survey

185. "Ground-Water Contamination by Hazardous Chemical Compounds Derived from Wood-Treatment Processes," W. E. Pereira and C. E. Rostad, U. S. Geological Survey

186. "Partitioning of Polycyclic Coal-Tar Constituents in a Two-Phase Ground-Water System," C. E. Rostad and W. E. Pereira, U. S. Geological Survey

187. "Applications of Semi-Micro HPLC to Environmental Analysis," S. M. McCown, Beckman/Altex

188. "Applications of Short Alkyl Chain, Wide Pore, Reverse Phase Packing in HPLC," M. May-Sheng Chan and J. S. Hobbs, Beckman/Altex

189. "High Speed Liquid Chromatographic Analysis of Synthetic Dyes," J. P. Chaytor, R. Heal, and J. S. Hobbs, Beckman/Altex

190. "HPLC Analysis of 2-(5-Cyanotetrazolato)Pentammine Cobal (III) Perchlorate (CP) on a Plyamide Column," R. J. Schumacher, Monsanto Research Corporation

191. "Kinetics of the Oxidation of Substituted Ferrocenes at Platinum and InP Electrodes," R. L. A. Pravata and C. A. Koval, University of Colorado

192. "Solid Sorbent Sampling of Sulfur Dioxide in Workplace Atmospheres," K. Irgum and M. Lindgren, University of Umea

193. "Microcomputer Based Data Acquisition and Reduction System for Ion Chromatography," R. K. Stahlhut and S. R. Bachman, Illinois State Water Survey

194. "Use of a Digital Recorder for Data Acquisition and Reduction in Thermal Analysis," J. R. Delmastro, Exxon Nuclear Idaho Company, Inc.

195. "The Use of a Dry Capillary Injection System in Trace Level Analysis of Diethylstilbestrol by Capillary GC/MS," W. J. Morris and G. J. Nandrea, U. S. Food & Drug Administration

196. "The Use of a Sequential Inductively Coupled Plasma-Atomic Emission Spectrometer for the Quality Control of Lead Smelter Operations," F. J. Szydlowski, J. Massa, and G. D. Haines, St Joe Lead Company

197. "Soil and Plant Concentrations of Cadmium and Zinc in the Vicinity of A Smelter," M. E. Farago and J. T. O'Connell, Royal Holloway and Bedford Colleges

198. "Platinum Metals and Plants: Location of Platinum Metals in Plant Tissues," M. E. Farago and P. J. Parsons, Royal Holloway and Bedford Colleges

199. "Development of a New FT-IR Spectrometer," J. P. Covey, and D. R. Mattson, Mattson Instruments

200. "High Speed Microcomputer for Fourier Transform Instruments," P. J. Coffey, and D. R. Mattson, Mattson Instruments

201. "A Novel Procedure for Implementing the Mole-Ratio Method," P. MacCarthy, A. Vella, and Z. D. Hill, Colorado School of Mines

202. "Laser Spectroscopy and Photophysics of Synthetic Photoreaction Centers," J. S. Connolly, Solar Energy Research Institute. J. R. Bolton, A. Siemarczuk, T. F. Ho, and A. C. Weedon, The University of Western Ontario

203. "Parameters Effecting Magnetic Field-Flow Fractionation of Metal Oxide Particles," T. C. Schunk, J. Gorse, and M. F. Burke, University of Arizona

204. "The Study of Small Particle Dispersions with Magnetic Field-Flow Fractionation," J. Gorse, T. C. Schunk, and M. F. Burke, University of Arizona

SYMPOSIUM ON ION CHROMATOGRAPHY

MONDAY AFTERNOON, AUGUST 15, 1983 - Second Floor, Room A
M. J. Fishman, Presiding

2:00 217. "A 12-Minute Isocratic Separation of Sulfite, Sulfate, and Thiosulfate by Single-Column Ion Chromatography (SCIC)," T. H. Jupille, D. W. Togami, and D. E. Burge, Wescan Instruments, Inc., Santa Clara, California

2:25 218. "Recycle Ion Chromatography for Trace Ions in Drinking Waters," T. B. Hoover and G. D. Yager, Environmental Protection Agency, Athens, Georgia

2:50 219. "Comparison of Ion Chromatography to Ion Analysis Methods Not Employing Eluent Modification," J. Stillian, C. A. Pohl, and E. L. Johnson, Dionex Corp., Sunnyvale, California

3:15 Break

3:40 220. "Oxidative Pyrolysis/Ion Chromatography - A Novel Approach to Organic Elemental Analysis," D. V. Vinjamoori, Monsanto Company, St. Louis, Missouri

4:05 221. "Ion Chromatographic Determination of Valproic Acid," H. Itoh and Y. Shinbori, Josai University, Sakado, Saitama, Japan

4:30 222. "Everything You Ever Wanted to Know About Boric Acid Analysis by IC," D. Eubanks, L. Angers, and A. W. Fitchett, Dionex Corp., Sunnyvale, California

SYMPOSIUM ON NUCLEAR MAGNETIC RESONANCE

MONDAY AFTERNOON, AUGUST 15, 1983 - Second Floor, Room C
NMR SESSION II

2:00 256. "Silicon-29 Spin Lattice Relaxation in Zeolites," R. D. Farlee, D. R. Corbin, and A. J. Vega, E. I. du Pont de Nemours & Company, Wilmington, Delaware

2:30 257. "NMR Studies of Adsorption in Zeolites," C. E. Bronnimann and G. E. Maciel, Colorado State University, Fort Collins, Colorado

3:00 258. "Zero Field NMR," D. P. Weitekamp, A. Bielecki, D. Zax, K. Zilm, and A. Pines, University of California, Berkeley, California

3:30 Break

4:00 259. "Recent Development in Two-Dimensional Solid State NMR," N. M. Szeverenyi, A. Bax, and G. E. Maciel, Colorado State University, Fort Collins, Colorado

4:30 260. "Physical and Chemical States of Small Molecules on Dispersed Noble Metal Surfaces. A CP NMR Study," H. B. Ragle and J. L. Ackerman, University of Cincinnati, Cincinnati, Ohio

SYMPOSIUM ON INFRARED SPECTROSCOPY

MONDAY AFTERNOON, AUGUST 15, 1983 - Third Floor, Room F
INFRARED SPECTROSCOPY - M. C. Goldberg, Presiding

12:55 Introduction - M. C. Goldberg

1:00 293. "Oriented Polychrystalline Films for Infrared Spectroscopic Studies," J. M. Landry and J. E. Katon, Miami University

1:30 294. "Infrared Study of Amorphous Silicon Nitride Films," J. P. Luongo, Bell Laboratories

2:00 295. "Some Practical Applications of Infrared Spectroscopy to Textiles," G. Celikiz, Philadelphia College of Textiles and Science

2:30 Break

3:00 296. "Infrared Spectroscopy of Complex Conversion Coatings," M. Kronstein, College of Mount St. Vincent

3:30 297. "Circular Variable Filter Characterization for Simulating Industrial Infrared Analyzer Response," R. B. Lam, A. A. D'Alessio, and S. Day, The Foxboro Co.

4:00 298. "Upgrading of Infrared Gas Analyzers for Process Control," D. P. Manka, Pittsburgh, Pennsylvania

4:30 299. "Infrared Studies on the Thermal Degradation of Poly(D_3-,1-^{13}C, and ^{15}N-Acrylonitriles)," J. J. Rafalko, Celanese Research Co.

SYMPOSIUM ON ATOMIC SPECTROSCOPY

TUESDAY MORNING, AUGUST 16, 1983 - Second Floor, Room F
J. Sneddon, Presiding

8:30 1. "Analysis of Dog Food and Related Biological Materials for Nutritional and Toxic Elements of Inductively Coupled Plasma (ICP) Spectrometry," J. Rasmuson and J. Mears, AMAX Extractive R&D, Golden, Colorado

8:50 2. "A Practical Means for Elimination of Certain Types of Stray Light in the Secondary Optics of an ICP-DRES System," T. Schmitt, Johnson Controls, Inc., St. Olaf College, Northfield, Minnesota

9:10 3. "Analysis of Steel for Sulfur, Phosphorus, and Boron by ICP Emission Spectrometry Using a Vacuum Monochromator," D. D. Nygaard, D. S. Chase, M. K. Conley, and D. A. Leighty, Instrumentation Laboratory Inc., Andover, Massachusetts

9:30 4. "Potassium Hydroxide/Potassium Superoxide as a Flux for ICP Analysis of Hazardous Waste Samples," J. Lowry, and E. Bour, Environmental Protection Agency (NEIC), Denver, Colorado. J. Rasmuson and R. Strode, Fred C. Hart Associates, Inc., Environmental Protection Agency (NEIC), Denver, Colorado

9:50 Break

10:20 5. "The Analysis of Geological Materials by a Scanning ICP Spectrometer," D. S. Chase, D. D. Nygaard, D. A. Leighty, and M. J. Conley, Instrumentation Laboratory, Inc., Andover, Massachusetts

10:40 6. "Determination of Rare Earth Elements in Geological Samples," J. Mears, C. O. Ingamells, and J. Rasmuson, AMAX Extractive R&D, Golden, Colorado

11:00 7. "The Use of Sodium Peroxide as a Sintering Agent for the ICP Analysis of Difficult Elements and Matrices," J. Rasmuson, J. Mears, G. Fogleman, and F. Pitard, AMAX Extractive R&D, Golden, Colorado

11:20 8. "A Multielement Preconcentration Method for Water Analysis by ICP/AA in Exploration Geochemistry," D. M. Hopkins, U. S. Geological Survey, Arvada, Colorado

SYMPOSIUM ON ELECTROCHEMISTRY

TUESDAY MORNING, AUGUST 16, 1983 - Third Floor, Room D
Session on Polymer-coated Electrodes - C. A. Koval, Presiding

9:00 66. "Thick-Polymer-Film Modified Electrodes - Potential Electrochromic Applications of Ring Substituted Bipyridine Metal Complexes," C. M. Elliott and J. G. Redepennning, Colorado State University, Fort Collins, Colorado

9:45 67. "Recent Developments in Phthalocyanine-Electrode Photoelectrochemistry," N. R. Armstrong, University of Arizona, Tucson, Arizona

10:30 Break

Electrochemistry General Session - C. M. Elliott, Presiding

11:00 68. "Metal and Metal Oxide Dispersed Particles for Electrocatalysis," T. Kuwana, Ohio State University, Columbus, Ohio

11:45 69. "The Direct Amperometric Detection of Carbohydrates and Amino Acids at Platinum Electrodes Applied to Liquid Chromatography," D. C. Johnson, S. Hughes, and J. Polta, Iowa State University, Ames, Iowa

SYMPOSIUM ON ENVIRONMENTAL CHEMISTRY

TUESDAY MORNING, AUGUST 16, 1983 - Third Floor, Room E
G. Aiken, Presiding

8:30 80. "Chemical Analysis of Dew and Frost Collected near Denver, Colorado," L. J. Schroder, M. M. Reddy, and A. B. Good, U. S. Geological Survey, Denver, Colorado

8:50 81. "Chemical Analysis of Sediment Coatings Using Selective Chemical Extraction and Inductively Coupled Argon Plasma," B. A. Kimball, U. S. Geological Survey, Lakewood, Colorado

9:10 82. "Atomic Absorption Spectrometry for Determination of Trace Metals in Organic Environmental Material after Different Sample Pretreatments," E. Scheubeck, H. Kunze, M. Pickel, L. Fischer, and L. Schon, Siemens Corp., Erlangen, FRG

9:30 83. "A Pneumatic Bottom Sediment Trap for Limnic Waters," G. H. Setlock, Rockwell International, Golden, Colorado

9:50 Break

10:10 84. "Cadmium Speciation in Natural Waters and Their Effect on Rainbow Trout," W. C. Gorman, Jr. and R. K. Skogerboe, Colorado State University, Fort Collins, Colorado. P. W. Davies, Colorado Division of Wildlife, Fort Collins, Colorado

10:30 85. "AB Initio Analysis of Hazardous Waste and Environmental Extracts," D. F. Gurka, U. S. Environmental Protection Agency, Quality Assurance Division. M. Hiatt, Region 9, Las Vegas, Nevada. R. Titus, University of Nevada at Las Vegas, Las Vegas, Nevada

10:50 86. "Unique Applications of Laser-Induced Fluorescence to Environmental Analysis," S. M. Klainer, ST&E Technical Services, Inc., San Ramon, California. T. Hirschfeld and F. P. Milanovich, Lawrence Livermore National Laboratory, Livermore, California

11:10 87. "Theoretical Applications of Multiple Compartment Passive Monitors," N. H. Price, UBTL, Salt Lake City, Utah

6TH INTERNATIONAL ELECTRON PARAMAGNETIC RESONANCE SYMPOSIUM

TUESDAY MORNING, AUGUST 16, 1983 - Second Floor, Room G
EPR SESSION III - H. van Willigen, Presiding

9:00 112. Plenary Lecture - "Time-Resolved ESR on Low-Dimensional Solids," M. Mehring, University of Stuttgart, Fed. Rep. Germany

9:50 113. "Spin Dynamics in Conducting Polymer Composites: Electron Spin Echo Studies of Polyacetylene in Polyethylene" H. Thomann, H. I. Kim, A. Morrobel-Sosa, C. Chiu, L. R. Dalton, M. E. Calvin, and G. E. Wnek, University of Southern California

10:20 Break

10:50 114. "Spin Lattice Relaxation in Quasi-One-Dimensional π-Electron Organic Semiconductors," B. Robinson and H. Thomann, University of Washington and University of Southern California

11:10 115. "Dipolar Correlation Functions and Spin Relaxation Rates for Finite Two-Dimensional Systems," J. -P. Korb and H. M. McConnell, C.N.R.S., France and Stanford University

11:25 116. "Magnetic Exchange Anisotropies as Determined by EPR," J. E. Drumheller, Montana State University

11:45 117. "EPR Investigation of the Cesium-Ammonia System," P. Hsu, W. Glaunsinger, K. Burton, and R. Catterall, Arizona State University and University of S. Salford

SYMPOSIUM ON FOURIER TRANSFORM INFRARED SPECTROSCOPY AND ITS APPLICATION

TUESDAY MORNING, AUGUST 16, 1983 - Third Floor, Room F
FTIR SESSION II - W. G. Fateley, Presiding

8:55 Introductory Remarks, W. G. Fateley

9:00 163. Plenary Lecture - "Fourier Transform Infrared Spectroscopy of Polymer Interfaces," J. L. Koenig, Case Western Reserve University, Cleveland, Ohio

9:45 164. "Effect of Chloride Contamination in Accelerating Photodegradation of Polymethylmethacrylate Films on Silver Surfaces," J. D. Webb, J. R. Pitts, T. M. Thomas, P. Schissel, and A. W. Czanderna, Solar Energy Research Institute, Golden, Colorado

10:05 165. "Polymer Film Degradation Mechanisms," C. Sergides, J. Hashim, A. R. Chughtai, and D. M. Smith, University of Denver. J. D. Webb, P. Schissel, and A. W. Czanderna, Solar Energy Research Institute, Golden, Colorado

10:25 Break

10:45 166. "FTIR as an Analytical Tool in a Polymer Laboratory," L. M. DiBello, Cryovac Div.; W. R. Grace & Co., Duncan, South Carolina

11:05 167. "Search for Sensitive FTIR Parameters for the Characterization of Acetylene-Terminated Resin Cure States," R. L. Levy, McDonnell Douglas Research Laboratories, St. Louis, Missouri

11:25 168. "Thermal Decomposition of Energetic Materials by Rapid Scan FTIR," T. B. Brill and R. J. Karpowicz, University of Delaware, Newark, Delaware

SYMPOSIUM ON ION CHROMATOGRAPHY

TUESDAY MORNING, AUGUST 16, 1983 - Second Floor, Room A
J. E. Girard, Presiding

8:30 223. "Determination of Low Concentrations of Monosaccharides, and Alcohols by Ion Chromatography with Pulsed Amperometric Detection," R. D. Rocklin, C. A. Pohl, E. L. Johnson, Dionex Corp., Sunnyvale, California

8:55 224. "Anion Analysis by Conventional HPLC," J. D. Newburger and W. R. Day, Waters Associates, Inc., Milford, Massachusetts

9:20 225. "Automated Ion Chromatography," S. H. Hoke, and L. J. Baxter, U. S. Army Medical Bioengineering Research and Development Laboratory, Ft. Detrick, Maryland

9:45 Break

10:15 226. "Automated Ion Chromatographic Determination of Anions in Precipitation Samples," G. S. Pyen, M. R. Brown, and D. E. Erdmann, U. S. Geological Survey, Doraville, Georgia

10:40 227. "Determination of Polyvalent Anions by Ion Chromatography," A. Woodruff, C. A. Pohl, and D. Eubanks, Dionex Corp., Sunnyvale, California

11:05 228. "Novel Applications of Ion Chromatography in Nuclear Power Generation," J. J. Law, Carolina Power and Light Company, Raleigh, North Carolina

SYMPOSIUM ON NUCLEAR MAGNETIC RESONANCE

TUESDAY MORNING, AUGUST 16, 1983 - Second Floor, Room C
NMR SESSION III

9:00 261. Plenary Lecture - "Probing Platinum Surfaces with NMR," C. P. Slichter, University of Illinois, Urbana-Champaign, Illinois

10:00 262. "MAR Studies of Crystallographic and NMR Properties," R. K. Harris, University of East Anglia, Norwich, England

10:40 Break

11:00 263. "Magnetic Resonance Studies of Acceptor Graphite Intercalation Compounds," H. A. Resing, G. R. Miller, L. Mattix, University of Maryland. M. J. Moran, Westchester State University. J. A. Milliken, Naval Research Laboratory, Washington D. C.

11:30 264. "^{19}F MAS-NMR and ^{19}F-^{31}P CP-MAS NMR of Fluoridated Hydroxyapatite Surfaces," J. P. Yesinowski, M. J. Mobley, and D. J. White, The Proctor and Gamble Company, Cincinnati, Ohio

SYMPOSIUM ON SURFACE ANALYSIS

TUESDAY MORNING, AUGUST 16, 1983 - Third Floor, Room A
B. F. Phillips, Presiding

9:00 Opening Remarks, B. F. Phillips

9:05 305. "Applied Surface Analysis - Present and Future," N. S. McIntyre, The University of Western Ontario, London, Ontario, Canada

9:45 306. "Quantitative Aspects of SIMS as a Depth Profiling Technique: Some Applications in Energy Research Programs," W. H. Christie, Oak Ridge National Laboratory, Oak Ridge, Tennessee

10:25 Break

10:45 307. "Rutherford Backscattering Analysis for Electronics Materials Characterization," M. D. Strathman, Charles Evans & Associates, San Mateo, California

11:25 308. "Design Considerations for a Dedicated Thin Film Analyzer Auger System," R. L. Gerlach, Perkin-Elmer Corporation, Eden Prairie, Minnesota

SYMPOSIUM ON ATOMIC SPECTROSCOPY

TUESDAY AFTERNOON, AUGUST 16, 1983 - Second Floor, Room F
T. M. Niemczyk, Presiding

1:30 9. Keynote Speaker - "Laser Enhanced Ionization Spectroscopy in Flames," R. B. Green, University of Arkansas, Fayetteville, Arkansas

2:10 10. "Plasma Mass Spectometry - A New Analytical Tool," D. J. Douglas, G. Rosenblatt, and E. S. Quan, SCIEX, Thornhill, Ontario, Canada. R. G. Smith, X-Ray Assay Laboratories, Ltd., Don Mills, Ontario, Canada

2:30 11. "A Theoretical Study of Atomic and Ionic Distributions in an Inductively Coupled Plasma," Kuang-pang Li, University of Lowell, Lowell, Massachusetts

2:50 Break

3:20 12. "The Analysis of Geological Matrices Via a Rapid Scanning High Resolution Plasma Emission Spectrometer System," W. J. Kinsey, R. C. Seeley, SpectraMetrics/Beckman Instruments, Inc., Andover, Massachusetts

3:40 13. "A Study of Interferences in D.C. Argon Plasma Emission Spectrometry," J. Sneddon and V. A. Fuavao, New Mexico State University, Las Cruces, New Mexico

4:00 14. "Fast Sequential Plasma Emission Spectroscopy: Recent Developments," A. W. Boorn, A. T. Zander, T. Karlinski, R. Bosshart, Beckman Instruments, Inc., Haverhill, Massachusetts

4:20 15. "The Application of Emulsifiers to Organic/Aqueous Matrices for DCP Analysis," R. R. Comtois, W. J. Kinsey, SpectraMetrics Inc., Andover, Massachusetts

4:40 16. "Oil Analysis Via a New Automatic Injection and Dilution System (AIDS) for ICP Emission Spectrometers," S. J. Evans and R. J. Klueppel, Baird Corporation, Bedford, Massachusetts

SYMPOSIUM ON ELECTROCHEMISTRY

TUESDAY AFTERNOON, AUGUST 16, 1983 - Third Floor, Room D
Electrochemistry General Session - C. M. Elliott, Presiding

2:00 70. "Efficient Nonaqueous Photoelectrochemical Cells," N. S. Lewis, Stanford University, Stanford, California

2:45 71. "Steric Effects in Electron Transfer Reactions of Transition Metal Complexes. I. Synthesis and Homogeneous Reactivity of Sterically-Hindered Redox Series," C. A. Koval, University of Colorado, Boulder, Colorado

3:05 72. "II. Kinetics of the Reduction of Co(III)(alkylamine)$_5$(X) Complexes at Mercury and Platinum Electrodes," M. E. Kettefer and C. A. Koval, University of Colorado, Boulder, Colorado

3:25 73. "III. Heterogeneous Electron Transfer Kinetics of Co(III,II), Fe(III,II), and Ru(III,II) Complexes Utilizing Square Wave Voltammetry," C. M. Reidsema and C. A. Koval, University of Colorado, Boulder, Colorado

3:45 Break

4:15 74. "Electrochemical In Situ Monitoring of Groundwater Parameters," J. A. Lanning, University of Colorado at Denver, Denver, Colorado

SYMPOSIUM ON ENVIRONMENTAL CHEMISTRY

TUESDAY AFTERNOON, AUGUST 16, 1983 - Third Floor, Room E
L. J. Schroder, Presiding

2:00 88. "Validation Study for the Fused Silica GC-Atmospheric Pressure Ionization-MS Method for the Isomer Specific Determination of 2,3,7,8-TCDD in Environmental Samples," W. A. Korfmacher, G. F. Moler, and R. K. Mitchum, National Center for Toxicological Research, Jefferson, Arkansas

2:20 89. "Effects of Aftertreatment Devices on the Physical, Chemical, and Biological Character of Diesel Particulate," J. P. Scholl, P. R. Miller, D. G. Leddy, S. T. Bagley, J. H. Johnson, and F. J. Hibbler, Michigan Technological University, Houghton, Michigan

2:40 90. "Chromatographic Patterns in Characterization of Synfuel By-Product Waters," D. A. Delistraty, J. M. Mason, F. G. Todd, L. M. Sebo, and R. E. Poulson, Laramie Energy Technology Center, Laramie, Wyoming

3:00 91. "Characterization of Water Composition during Discharge from Hydrostatic Testing of Natural Gas Pipelines," G. A. Eiceman, B. D. Baker, and C. S. Leasure, New Mexico State University, Las Cruces, New Mexico

3:20 Break

3:40 92. "Comparative Study of the Organic and Inorganic Composition of El Chichon and Mount St. Helens Ashes," J. R. Garbarino, U. S. Geological Survey, Lakewood, Colorado

4:00 93. "A Comprehensive Radiological Emergency Surveillance Program near Nuclear Power Plants," J. J. Kliment, Wilmington Laboratory, Delaware Department of Natural Resources and Environmental Control, Wilmington, Delaware

6TH INTERNATIONAL ELECTRON PARAMAGNETIC RESONANCE SYMPOSIUM

TUESDAY AFTERNOON, AUGUST 16, 1983 - Second Floor, Room G
EPR SESSION IV - S. S. Eaton, Presiding

1:30 118. Plenary Lecture - "ESR and ENDOR Investigations of Stable Free Radicals Formed From Sulphur-Nitrogen Heterocycles," L. H. Sutcliffe, The University, Liverpool

2:30 119. "Nuclear Quadrupolar Interactions in Electron Spin Echo Spectra of Solids," M. Bowman, Argonne National Laboratory

EPR SESSION V - S. S. Eaton, Presiding

Poster Session - Authors present 3:00 - 4:00 for papers labeled A.
4:00 - 5:00 for papers labeled B.

A 120. "ESR Spectra, Chemical Properties and Spin Probe Potential of a Series of Disulphenimidyl Free Radicals," S. R. Harrison, R. S. Pilkington, and L. H. Sutcliffe, The University, Liverpool

B 121. "An Electron Spin Resonance Study of Organo-Sulfur Radicals Produced in Electron-Irradiated Aqueous Solutions. Spin Trapping With Nitromethane Aci-Anion and 2-methyl-2-nitrosopropane," H. Taniguchi, University of Notre Dame

A 122. "Site Location of the Trapped Electron in X-ray Irradiated Single Crystals of Rhamnose and Trehalose," L. D. Kispert, P. -O. Samskog, and A. Lund, University of Alabama and Studsvik Research Laboratory, Sweden

B 123. "EPR of Thermal Decomposition Products From Energetic Materials," M. D. Pace, A. D. Britt, and W. B. Moniz, Naval Research Laboratory

A 124. "Magnetic Resonance Studies of Native and Carbonized Illinois Coal," R. B. Clarkson and E. Duliba, University of Illinois

B 125. "EPR Study of a Monotropic Liquid Crystal HBT," S. K. Gupta and R. Rai, National Physical Laboratory, New Delhi

A 126. "Temperature Dependent Vibronic Effect in the EPR of a Solid Mixed Valence Benzotriazolato Copper Complex," J. Baranowski, F. Padula, C. Goldstein, G. Kokoszka, and A. Siedle, SUNY Plattsburgh and 3M Central Research Laboratory

B 127. "Jahn-Teller Effect in $Cu(N_6C_{12}H_{30})(ClO_4)_2 \cdot C_6H_6$," G. Kokoszka, Burmeister, SUNY Plattsburgh and University and Delaware

A 128. "The Nature of the Jahn-Teller Effect in the Copper Doped Hexamidazole Zinc Dichloride Tetrahydrate Complex," E. de Boer, C. P. Keijzers, T. Jansen, G. van Kalkeren, and J. S. Wood, University of Nijmegen

B 129. "Single Crystal EPR Spectra of Spin-Labeled Metalloporphyrins," R. Damoder, K. M. More, G. R. Eaton, and S. S. Eaton, University of Denver and University of Colorado at Denver

A 130. "Spin-Labeled Complexes of Iron(III) and Nickel(II)," L. Fielding, K. M. More, P. Smith, G. R. Eaton, and S. S. Eaton, University of Denver and University of Colorado at Denver

B 131. "Drug Mediated Superoxide Production," G. M. Rosen, Duke University Medical Center

A 132. "Characterization of Motion of ^{15}N-Substituted Stearic Acid Spin Labels Bound to Proteins and Membrane Bilayers," J. H. Park, S. D. Venkataramu, C. R. Park, N. Abumrad, and A. H. Beth, Vanderbilt University

B 133. "The Effects of Internal Motion on EPR Spectra in the Slow and Ultra Slow Motional Regimes," B. Robinson and A. H. Beth, University of Washington and Vanderbilt University

A 134. "Spin Trapping and Direct Electron Spin Resonance Investigations of the Photoreduction of Gentian (Crystal) Violet," V. Fischer, W. G. Harrelson Jr., C. F. Chignell, and R. P. Mason, NIEHS, Research Triangle Park

B 135. "Synthesis and EPR Studies of Chiral Dinitroxide Crown Ethers," H. Dugas, M. Ptak, P. Keroack, University of Montreal and CNRS, France

SYMPOSIUM ON ION CHROMATOGRAPHY

TUESDAY AFTERNOON, AUGUST 16, 1983 - Second Floor, Room A
R. M. Merrill, Presiding

2:00 229. "Plating Bath Analysis by Ion Chromatography," K. K. Haak, Dionex Corp., Sunnyvale, California

2:25 230. "Determination of Ionic Species of Clinical Significance in Cerebrospinal Fluid by High Performance Ion Chromatography Using Conductometric Detection," M. S. Davis, LDC/Milton Roy, Riviera Beach, Florida

2:50 231. "Professional Society Involvement with Ion Chromatography," A. W. Fitchett, T. H. Jupille, and M. J. Fishman

3:10 Break

3:40 232. "High-Speed Action Separations by Single-Column Ion Chromatography (SCIC)," D. W. Togami, T. H. Jupille, and D. E. Burge, Wescan Instruments, Inc., Santa Clara, California

4:05 233. "Determination of Carboxylate Anions by Ion Chromatography," G. Hennion and C. A. Pohl, Dionex Corp., Sunnyvale, California

SYMPOSIUM ON NUCLEAR MAGNETIC RESONANCE

TUESDAY AFTERNOON, AUGUST 16, 1983 - Second Floor, Room C
NMR SESSION IV

2:00 265. "^{113}Cd NMR Studies of Cadmium Oxide," M. P. Shatlock and G. E. Maciel, Colorado State University, Fort Collins, Colorado

2:30 266. "^{15}N NMR Studies of Adsorbed Pyridine," B. L. Hawkins, J. F. Haw, I.-S. Chuang, and G. E. Maciel, Colorado State University, Fort Collins, Colorado

3:00 267. "CP MAS-NMR Studies of the Synthesis of $(H^{13}C^{15}N)_x$ Polymers," R. A. McKay, J. Schaefer, and E. O. Stejskal, Monsanto Company, St. Louis, Missouri. R. Ludicky, and C. N. Matthews, University of Illinois at Chicago, Chicago, Illinois

3:30 Break

Poster Session - Authors present 4:00 - 5:00 for papers

268. "Fluorine-19 NMR Investigation of Boron Trifluoride-Monethylamine," R. E. Smith and F. Larsen, Bendix Corp., Kansas City, Missouri

269. "Identify that Terpene (with Computer Assisted NMR Interpretation)," M. Hagedorn, International Flavors and Fragrances, Union Beach, New Jersey

270. "Solid State ^{2}D-NMR Studies of the Dynamics of ND_2 Groups in Amino Acids," A. Reuveni, University of Washington, Seattle, Washington

271. "Experiments Using ^{33}S NMR," P. S. Belton, I. J. Cox, and R. K. Harris, University of East Anglia, Norwich, England

272. "Estonia Oil Shale Kerogen NMR and Structure," E. Lippmaa, Estonian Academy of Sciences, Tallinn, Estonia, USSR

273. "Two Dimensional ^{13}C NMR of Solids," A. C. Lind, and D. A. Cornell, McDonnell Douglas, Research Laboratories, St. Louis, Missouri

274. "Structural Assignments of O-Sulfate Esters and Glucuronide Metabolites of Epinine by High Field Proton NMR," G. Y. Kuo, D. B. Staiger, and B. Y-H. Hwang, Smith Kline & French Laboratories, Philadelphia, Pennsylvania

275. "Variable-Temperature ^{13}C Solid State NMR as a Probe of Polycarbonate-Diluent Interactions," L. A. Belfiore, Colorado State University, Fort Collins, Colorado. S. L. Cooper, University of Wisconsin, Madison, Wisconsin

276. "NMR Outside the RF Coil and Outside the Magnet?," A. Rath, and S. B. W. Roeder, San Diego State University, San Diego, California. E. Fukushima, The Los Alamos National Laboratory, Los Alamos, New Mexico

SYMPOSIUM ON INFRARED SPECTROSCOPY

TUESDAY AFTERNOON, AUGUST 16, 1983 - Third Floor, Room F
INFRARED SPECTROSCOPY - J. R. Riter Jr., Presiding

1:45 "Introduction - J. R. Riter, Jr.

2:00 300. "The Transformation Matrices of Symmetry Operations Used in Infrared Spectroscopy," P. G. Bourne, Scott Paper Co.

2:30 301. "Vibrational Spectra of Conformations of Substituted Cyclopropane Derivatives," V. F. Kalasinsky, Y. Y. Yeh, Mississippi State University. C. J. Wurrey, University of Missouri

3:00 302. "Infrared Photoacoustic and Diffuse Reflectance Spectroscopy of Absorbed Pesticides," D. J. Gerson, IBM Instruments, Inc. W. G. Fately, Kansas State University

3:30 Break

4:00 303. "Computerized Infrared Identification (CIRID) Program in Pharmaceutical Control Laboratory," R. S. Chao, D. A. Hatzenbuhler, R. G. Richman, J. M. Winkworth, and A. M. Richter, The Upjohn Co.

4:30 304. "Computerized Infrared Spectral Identification," C. D. Craver, Chemir Laboratories

SYMPOSIUM ON SURFACE ANALYSIS

TUESDAY AFTERNOON, AUGUST 16, 1983 - Third Floor, Room A
W. H. Christie, Presiding

2:00 309. "CRISS, An NSF Regional Instrumentation Facility and Synchrotron Radiation Facilities," G. J. Lapeyre, J. R. Anderson, and D. J. Frankel, Montana State University, Bozeman, Montana

2:20 310. "Instrumental Effects on ESCA Spectroscopic Information," T. W. Rusch and J. S. Hammond, Perkin-Elmer Corporation, Eden Prairie, Minnesota

2:40 311. "*Analysis of Corrosion Products on Stainless Steel Surface* - Correlative Use of Auger, SIMS, and Radioactive Implant Studies," N. S. McIntyre, W. J. Chauvin, D. Johnston, F. E. Doern, The University of Western Ontario, London, Ontario, Canada. E. McAlpine, and D. Lister, Chalk River Nuclear Laboratories, Chalk River, Ontario, Canada

3:00 Break

3:20 312. "Applications of Complementary Microprobe Analyses to Photovoltaic Devices," L. L. Kazmerski, Solar Energy Research Institute, Golden, Colorado

3:40 313. "Compositional Integrity of the $CuInSe_2$ Bilayer in a Cd(Zn)S/$CuInSi_2$ Solar Cell," T. P. Massopust, L. L. Kazmerski, and P. J. Ireland, Solar Energy Research Institute, Golden, Colorado

4:00 314. "Leaching Properties and Surface Studies of a Glass Prepared with Radioactive Zirconia Calcine," D. A. Pavlica, B. A. Stapes, and H. S. Cole, Exxon Nuclear Idaho Company, Inc., Idaho Falls, Idaho

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SYMPOSIUM ON ATOMIC SPECTROSCOPY

WEDNESDAY MORNING, AUGUST 17, 1983 - Second Floor, Room F
D. M. Mehs, Presiding

9:00 17. "The Reduction of Interferences in Graphite Furnace Atomic Absorption," M. A. Cunliffe and D. E. Shrader, Varian Instrument Group, Park Ridge, Illinois

9:20 18. "New Atomic Absorption Background Correction Technique," S. B. Smith, Jr., R. G. Schleicher, and M. J. Conley, Instrumentation Laboratory, Inc., Andover, Massachusetts. G. M. Heiftje, Indiana University, Bloomington, Indiana

9:40 19. "Graphite Tube Atomizer Performance-ASTM Graphite Furnace Round Robin for Furnace," M. A. Cunliffe, L. M. Voth, and D. E. Shrader, Varian Instrument Group, Park Ridge, Illinois

10:00 Break

10:30 20. "Determination of Selenium in Horse Blood by Hydride Generated Flame Atomic Absorption Spectrophotometry," J. Sneddon and B. L. Porter, New Mexico State University, Las Cruces, New Mexico

10:50 21. "Isotope Determinations by Atomic Absorption Spectroscopy: Theory and Simulation," K. A. S. Pathiratne and R. J. Lovett, North Dakota State University, Fargo, North Dakota

11:10 22. "Determination of Metals in Complex Matrices by Forming Volatile Metal Chlorides," R. W. Chong and R. K. Skogerboe, Colorado State University, Fort Collins, Colorado

SYMPOSIUM ON ENVIRONMENTAL CHEMISTRY

WEDNESDAY MORNING, AUGUST 17, 1983 - Third Floor, Room E
J. R. Garbarino, Presiding

8:30 94. "Measurements of the Vertical Flux and Mean Concentration Budget for Ozone in a Convective Boundary Layer," R. Pearson, Jr., Colorado State University, Fort Collins, Colorado. D. H. Lenschow and B. B. Stankov, National Center for Atmospheric Research, Boulder, Colorado

8:50 95. "Turbulent Fluxes of Ozone, Heat and Moisture over Forest," S. R. Kawa and R. Pearson, Jr., Colorado State University, Fort Collins, Colorado. D. H. Lenschow and B. B. Stankov, National Center for Atmospheric Research, Boulder, Colorado

9:10 96. "Measurement of Mean Concentration and Transport of Ozone in Small Cumuli during CCOPE," C. J. Weaver and R. Pearson, Jr., Colorado State University, Fort Collins, Colorado

9:30 97. "The Effects of Photochemical Reactions on the Vertical Fluxes of O_3, NO, and NO_x in the Atmospheric Surface Layer: A Field Study," B. L. Woodruff and R. Pearson, Jr., Colorado State University, Fort Collins, Colorado. A. C. Delany, G. J. Dolan, D. R. Fitzjarrald, D. H. Lenschow, F. L. Melchor, and A. F. Wartburg, National Center for Atmospheric Research, Boulder, Colorado

9:50 Break

10:10 98. "Nitrogen Oxides in Urban Atmospheres," L. G. Anderson. University of Colorado at Denver, Denver, Colorado

10:30 99. "The Emission of Organic Air Pollutants from Shale Oil Wastewaters," S. B. Hawthorne and R. E. Sievers, University of Colorado, Boulder, Colorado

10:50 100. "The Change in Organic Composition of Oil Shale WasteWater by Tertiary Treatment Techniques," M. K. Conditt and R. E. Sievers, University of Colorado, Boulder, Colorado

11:10 101. "Removal of Organic Air Pollutants by Precipitation," R. S. Hutte and R. E. Sievers, University of Colorado, Boulder, Colorado

11:30 102. "Ambient Nitric Acid Measurements-Interference from Pan and Organo-nitrogen Compounds," R. L. Tanner, Yin-Nan Lee, T. J. Kelly, and J. S. Gaffney, Brookhaven National Laboratory, Upton, New York

11:50 103. "How to Keep Mercury in the +2 Valence State in Aqueous Solution," J. L. Robinson, Environmental Protection Agency, Kansas City, Kansas

6TH INTERNATIONAL ELECTRON PARAMAGNETIC RESONANCE SYMPOSIUM

WEDNESDAY MORNING, AUGUST 17, 1983 - Second Floor, Room G
EPR SESSION VI - S. S. Eaton, Presiding

9:00 136. Plenary Lecture - "Recent Advances in Solid State ENDOR Methodology," A. Schweiger, ETH-Zurich

EPR Session VII - S. S. Eaton, Presiding

Poster Session - Authors present 10:00 - 11:00 for papers labeled C
11:00 - 12:00 for papers labeled D

C 137. "Recent Progress in Solution-ENDOR Spectroscopy of Non-Proton Nuclei," W. Lubitz, Free University, Berlin

D 138. "ENDOR Study of Photo-Excited Triplets Randomly Oriented in Solid Solution," T. K. Chandrashekar, B. Kirste, and H. van Willigen, University of Massachusetts at Boston

C 139. "A Reinvestigation of the Conformational Interconversion in 1,2,3,6,7,8-Hexahydropyrene Cation Radical by EPR and ENDOR," M. Vuolle and R. Makela, University of Jyvaskyla

D 140. "Time Resolved Fluorescence Detected Magnetic Resonance (FDMR) of Transient Radical Ions," S. M. Lefkowitz and A. D. Trifunac, Argonne National Laboratory

C 141. "Bioinorganic Model Systems: EPR of 5 Coordinate Cu(II) Complexes with Tripod Ligands," F. Padula, C. Goldstein, G. Kokoszka, K. Karlin, J. Hayes, and J. Zubieta, SUNY Plattsburgh and SUNY Albany

D 142. "Low Spin Ferric Porphyrin Complexes: Analysis of the Electronic Structure Based on Single-Crystal EPR Measurements," M. P. Byrn, B. A. Katz, N. L. Keder, K. R. Levan, C. J. Magurany, K. M. Miller, J. W. Pritt, and C. E. Strouse, University of California, Los Angeles

C 143. "An EPR Investigation of $[Co(III)(TPP)]^{2+}$ Cation Radicals: Anion and Solvent Dependence of the EPR Spectra," K. Ichimori, H. Ohya-Nishiguchi, N. Hirota, and K. Yamamoto, Kyoto University and Institute for Physical and Chemical Research, Japan

D 144. "Dipole-dipole Interaction Between Cupric Ion and Human Met-Hemoglobin," W. E. Antholine, R. Basosi, and F. Taketa, Medical College of Wisconsin

C 145. "Low Frequency, S-Band, EPR for Cupric Bleomycin," W. E. Antholine, J. S. Hyde, and D. H. Petering, Medical College of Wisconsin and University of Wisconsin, Milwaukee

D 146. "Electron Spin Echo Studies of Spin-Spin Interactions in Cytochrome c Oxidase," R. LoBrutto, G. Goodman, and J. S. Leigh, Johnson Research Foundation and University of Pennsylvania

C 147. EPR-Detectable Active Site Derivatives of the Coupled Binuclear Copper Protein Hemocyanin," D. E. Wilcox, W. B. Mims, and E. I. Solomon, Stanford University and Bell Laboratories

D 148. "ESR Study of Intramolecular Exchange of Metal Ions in Alterdentate Ligands," C. Daul, E. Deiss, J. -N. Gex, D. Perret, D. Schaller, and A. von Zelewsky, Institute of Inorganic Chemistry, Fribourg

C 149. "Analysis and Interpretation of EPR and ZFR (Zero Field Resonance) of Mn(II) in Tutton Salts," S. J. Strach and R. Bramley, Australian National University

D 150. "EPR of Fe(III) in Spodumene. Analysis of the Structure Distortion Around Fe(III) by Means of the Superposition Model," J. M. Gaite, UER Sciences, France

C 151. "ESR of Heavy Metal Defects in Alkali Halides and Application to Color Center Lasers," D. Schoemaker, University of Antwerp

D 315. "Ligand Hyperfine Spectra of Cu^{+2} in AgCl," W. B. Paul, L. Rowan, L. Slifkin, University of North Carolina

SYMPOSIUM ON FOURIER TRANSFORM INFRARED SPECTROSCOPY AND ITS APPLICATION

WEDNESDAY MORNING, AUGUST 17, 1983 - Third Floor, Room F
FTIR SESSION III - J. L. Koenig, Presiding

8:55 Introductory Remarks, J. L. Koenig

9:00 169. Plenary Lecture - "Diffuse Reflectance FT-IR Spectrometry: A Powerful Tool for the Study of Powdered Samples," P. R. Griffiths, University of California, Riverside, California

9:40 170. Plenary Lecture - "Dilemma: Transmission, ATR, DRIFTS or PAS Studies by FT-IR?," J. Graham and W. G. Fateley, Kansas State University, Manhattan, Kansas. J. Casper, IBM Instruments, Inc., Danbury, Connecticut

10:20 Break

10:40 171. "Precision Better than 1 MHz in Fourier Spectroscopy Below 1000 cm^{-1}," J. Kauppinen, V-M. Horneman, and E. Kyrö, University of Oulu, Finland

11:00 172. "Use of FTIR as a General Laboratory Support Instrument," W. Wasson, AFWL/SUE, Kirtland AFB, New Mexico

11:15 173. "An FT-IR in the Open Lab Concept," J. W. Ryan, B. F. Goodrich Company, Avon Lake, Ohio

11:35 174. "Methods of Analysis of Tablet Contents by FTIR," D. C. Peters, Analect Instruments, Utica, New York. J. W. Mohar, Analect Instruments, Irvine, California

GENERAL SESSION

WEDNESDAY MORNING, AUGUST 17, 1983 - Third Floor, Room A
E. A. Brovsky Presiding

8:55 Introductory Remarks, E. A. Brovsky

9:00 205. "A New Nitrogen Analyzer for Rapid and Accurate Nitrogen Determination," T. M. Jackson, Erba Instruments, Inc., Peabody, Massachusetts

9:30 206. "Innovative Wet-Air Oxidation Treatment of Selected Wastewaters by the Vertical Tube Reactor," C. B. Cassetti and B. K. Kent, Applied Science & Engineering, Inc., Englewood, Colorado

10:00 Break

10:30 207. "A Direct Calculational Technique for Making Corrections for Corrigible Systematic Error in Analytical Results," M. J. Cardone and J. G. Lehman, Norwich Eaton Pharmaceuticals, Inc., Norwich, New York

10:45 208. "An Electronic Transducer for the Automated Determination of Integrated Gas Volumes," C. Hyndman and M. Bader, Moravian College, Bethlehem, Pennsylvania

11:10 209. "Use of Standard Additions in Natural Water Systems," W. C. Gorman, Jr. and R. K. Skogerboe, Colorado State University, Fort Collins, Colorado. P. W. Davies, Colorado Division of Wildlife, Fort Collins, Colorado

11:30 210. "Ion Exchange Studies of Metal-Multiligand Equilibria," T. F. Rees, S. R. Daniel, G. C. Smith, and P. MacCarthy, Colorado School of Mines, Golden, Colorado

SYMPOSIUM ON ION CHROMATOGRAPHY

WEDNESDAY MORNING, AUGUST 17, 1983 - Second Floor, Room A
G. S. Pyen, Presiding

8:30 234. "Improved Fiber Suppressors for Expanded IC Capabilities," R. Slingsby, C. A. Pohl, Dionex Corp., Sunnyvale, California

8:55 235. "The Determination of Nitrogen in Silicate Based Nitride Glasses Using Cation Chromatography," R. M. Merrill, Sandia National Laboratories, Albuquerque, New Mexico

9:15 236. "High Performance Liquid Chromatographic Analysis of Anions and Cations in Soils," K. L. Fitzpatrick and W. T. Frankenberger, Jr., University of California, Riverside, California

9:40 Break

10:10 237. "Chemical Analysis of Fluid Inclusions by Ion Chromatography," J. M. Thompson, S. S. Howe, and W. E. Hall, U. S. Geological Survey, Menlo Park, California

10:30 238. "The Determination of Fluroacetic Acid by Ion Chromatography," R. C. Buechele, FBI Academy, Quantico, Virginia

10:55 239. "Ion Chromatography of Transition Metals," J. Riviello, C. A. Pohl, Dionex Corp., Sunnyvale, California

MASS SPECTROSCOPY

WEDNESDAY MORNING, AUGUST 17, 1983 - Third Floor, Room D
M. B. Bergeron, Presiding

8:55 Introductory Remarks, M. B. Bergeron

9:00 246. "Analysis of Progesterone and Metabolites from Breast Cancer Cells by GC and GC-MS," A. W. Pike, K. Horwitz, and P. V. Fennessey, University of Colorado School of Medicine, Denver, Colorado

9:15 247. "Applications of an RPN Stack-Structured Environment for GC/MS Data," R. K. Latven, Hewlett-Packard Company, Santa Clara, California

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9:30 248. "High Resolution Fast Atom Bombardment Mass Spectrometry with a Multichannel Analyzer," K. L. Clay and R. C. Murphy, University of Colorado Medical Center, Denver, Colorado

10:00 249. "Analysis in Human Metabolism of Stable Isotopes of Trace Metals," C. Moynihan and P. V. Fennessey, University of Colorado School of Medicine, Denver, Colorado

10:30 Break

11:00 250. "A Reduced Pressure Microwave Plasma Source for Mass Spectrometric Analysis," S. K. MacLeod and R. K. Skogerboe, Colorado State University, Fort Collins, Colorado. L. R. Layman and F. E. Licthe, U. S. Geological Survey, Denver, Colorado

11:30 251. "Memory Effects in Mass Spectrometric Analysis of Volatile Metal Chelates," S. K. Macleod and R. K. Skogerboe, Colorado State University, Fort Collins, Colorado

SYMPOSIUM ON NUCLEAR MAGNETIC RESONANCE

WEDNESDAY MORNING, AUGUST 17, 1983 - Second Floor, Room C
NMR SESSION V

8:30 277. "The Structure of Amorphous Films Containing Tri-P-Tolylamine and Bisphenol-A-Polycarbonate as Determined by High-Resolution ^{13}C NMR of Partially Deuterated Samples," J. M. Hewitt, P. M. Henrichs, M. Scozzafava, R. P. Scaringe, M. Lindner, and L. J. Sorriero, Eastman Kodak Company, Rochester, New York

9:00 278. "A ^{2}H NMR Analysis of the Molecular Origin of Thermal Transitions in Polycarbonates," P. B. Smith, R. A. Bubeck, and S. E. Bales, Dow Chemical Company, Midland, Michigan

9:30 279. "Solution and Solid State NMR Studies of Polycarbonates and Polysulfones," D. Cory, P. Klein, W. Ritchey, and Y. T. Shieh, Case Western Reserve University, Cleveland, Ohio

10:00 Break

10:30 280. "^{13}C NMR Studies of Solid Plant Material," J. F. Haw and G. E. Maciel, Colorado State University, Fort Collins, Colorado

11:00 281. "Solid State NMR Characterization of Carbonaceous Chondrites," J. F. Frye, Colorado State University, Fort Collins, Colorado. J. Cronin, University of Arizona, Tucson, Arizona

11:30 282. "Recent Progress ^{13}C NMR Analysis of Solid Fossil Fuels," G. E. Maciel, N. M. Szeverenyi, M. Sardashti, and M. Davis, Colorado State University, Fort Collins, Colorado

SYMPOSIUM ON ATOMIC SPECTROSCOPY

WEDNESDAY AFTERNOON, AUGUST 17, 1983 - Second Floor, Room F
T. M. Niemczyk, Presiding

1:30 23. "The Cooled Hollow Cathode Discharge," K. Burton and D. Mehs, Fort Lewis College, Durango, Colorado

1:50 24. "Determination of Beryllium on Filters from Air Sampling," J. L. Long, Rockwell International, Rocky Flats Plant, Energy Systems Group, Golden, Colorado

2:10 25. "Atomic Absorption Analysis of Fine and Coarse Airborne Dust," S. P. Kelty and C. J. Weschler, Bell Laboratories, Holmdel, New Jersey

2:30 26. "Determination of Trace Metals Using Organic Extraction/Graphite Furnace AAS," I. Yin, M. Robles, and T. M. Niemczyk, University of New Mexico, Albuquerque, New Mexico

2:50 27. "Innovative Modifications to the Delves Cup Blood-Lead Analysis Procedure," P. Taylor, GM Technical Center, Warren, Michigan

6TH INTERNATIONAL ELECTRON PARAMAGNETIC RESONANCE SYMPOSIUM

WEDNESDAY AFTERNOON, AUGUST 17, 1983 - Second Floor, Room G
EPR SESSION VIII - G. Kokoska, Presiding

2:00 152. Plenary Lecture - "Electron Spin Echo Spectroscopy of Biological Materials," J. Peisach and W. B. Mims, Albert Einstein College of Medicine and Bell Laboratories

2:50 153. "Accessibility of the Active Sites in Metalloproteins to Solvent as Determined by Electron Spin Echo Envelope Spectroscopy," W. B. Mims, J. Peisach, and J. L. Davis, Bell Laboratories and Albert Einstein College of Medicine

3:20 Break

3:50 154. "The Use of Swept-Frequency EPR at Zero and Non-Zero Applied Magnetic Field," S. J. Strach and R. Bramley, Australian National University

4:10 155. "ESR at Low Fields for Noninvasive Diagnosis, L. J. Berliner and H. Nishikawa, Ohio State University

4:30 156. Plenary Lecture - "Study of Superslow Rotation of Nitroxide Radicals Using Pulse ELDOR (electron spin echo spectrometer)," K. Salikov, Institute of Chemical Kinetics and Combustion, USSR

5:00 Closing Remarks - G. R. Eaton

SYMPOSIUM ON FOURIER TRANSFORM INFRARED SPECTROSCOPY AND ITS APPLICATION

WEDNESDAY AFTERNOON, AUGUST 17, 1983 - Third Floor, Room F
FTIR SESSION IV - P. R. Griffiths, Presiding

1:55 Introductory Remarks, P. R. Griffiths

2:00 175. Plenary Lecture - "Some Uses of Infrared Photothermal Beam Deflection Spectroscopy," M. J. D. Low, New York University, New York City, New York

2:50 176. "The Study of Oxide Films on Metals Using FTIR Reflectance Spectroscopy," D. K. Ottesen, L. R. Thorne, and A. S. Nagelberg, Sandia National Laboratories, Livermore, California

3:10 177. "An Infrared and EPR Study of Impure Zinc Oxide," D. J. Gladstone, A. R. Chughtai, and D. M. Smith, University of Denver, Denver, Colorado

3:30 Break

3:50 178. "Aqueous Reverse Phase LC/FTIR Developments and Applications," K. S.Kalasinsky, J. T. McDonald, and V. F. Kalasinsky, Mississippi State Chemical Laboratory and Mississippi State University, Mississippi State, Mississippi

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4:10 179. "An HPLC-FTIR Interface with Submicrogram Detection Limits for Both Reverse Phase and Normal Phase Chromatography," P. J. Duff, USA Ballistic Research Laboratory, DRDAR-BLI, Aberdeen Proving Ground, Maryland. P. R. Griffiths, University of California, Riverside, California

4:40 180. "Isolation and Molecular Identification of Ultramicro Contaminants by Fourier Transform Infrared Spectroscopy," M. E. Lacy, Rockwell International, Anaheim, California

SYMPOSIUM ON ION CHROMATOGRAPHY

WEDNESDAY AFTERNOON, AUGUST 17, 1983 - Second Floor, Room A
M. J. Fishman, Presiding

2:00 240. "Analysis of Bromide in Foods by Single-Column Ion Chromatography (SCIC)," D. W. Togami, T. H. Jupille, and D. E. Burge, Wescan Instruments, Inc., Santa Clara, California

2:25 241. "The Characterization of Some Low Explosive Residues by Ion Chromatography," T. L. Rudolph, and E. C. Bender, FBI Laboratory, Washington, D. C.

2:50 242. "On-Line Ion Chromatographic Analysis of High Purity Water Systems at Nuclear Power Plants," M. N. Robles and J. L. Simpson, General Electric Company, San Jose, California

3:10 Break

3:40 243. "Sampling and Analysis of Airborne Inorganic Particulates from Southeastern Las Vegas Basin," R. W. Davis, Stauffer Chemical Company, Richmond, California

4:05 244. "Use of the I^2C Approach for Assay Level Ion Chromatographic Analysis," A. W. Fitchett, C. A. Pohl, and E. L. Johnson, Dionex Corp. Sunnyvale, California

4:30 245. "The Monitoring of Electroless Copper Plating Solutions Using Ion Chromatographic Exclusion," L. C. Yeager and J. W. Basinger, Lockheed Missiles and Space Company, Inc., Sunnyvale, California

SYMPOSIUM ON NUCLEAR MAGNETIC RESONANCE

WEDNESDAY AFTERNOON, AUGUST 17, 1983 - Second Floor, Room C
NMR SESSION VI

2:00 283. "Mapping Chemical Reactions in Coal by CP/MAS ^{13}C NMR Spectroscopy," E. Hagaman, Oak Ridge National Laboratory, Oak Ridge, Tennessee

2:30 284. "NMR of Viruses," S. J. Opella, University of Pennsylvania, Philadelphia, Pennsylvania

3:00 Break

3:30 285. "NMR and Spectroscopic Studies of Metal Ion Binding Sites of α-Lactalbumin," L. J. Berliner, K. Murakami, and H. Nishikawa, Ohio State University, Columbus, Ohio

4:00 286 "Orientation Dependent NMR and EPR Spectra of Plant Leaves," D. C. McCain, University of Southern Mississippi, Hattiesburg, Mississippi. J. L. Markley, Purdue University, West Lafayette, Indiana

4:30 287. "Copper and Nickel Binding to Serum Albumins by Chloride NMR," P. Mohanakrishnan, University of Alberta, Edmonton, Alberta, Canada. R. H. Cox, Phillip Morris Research Center, Richmond, Virginia. C. F. Chignell, NIEHS, Research Triangle Park, North Carolina

1 ANALYSIS OF DOG FOOD AND RELATED BIOLOGICAL MATERIALS FOR NUTRITIONAL AND TOXIC ELEMENTS OF INDUCTIVELY COUPLED PLASMA (ICP) SPECTROMETRY. J. Rasmuson and J. Mears, AMAX Extractive R&D, 5950 McIntyre Street Golden, CO 80403.

A modified wet-ash ICP procedure for the analysis of high aluminum and silica-content foods and biological materials will be discussed. The adequacy of conventional wet-ashing and the modified procedure will be evaluated based on the analysis of standard reference materials, residues after dissolution, and spike recoveries. A brief review of the literature on this subject will also be presented.

2 A PRACTICAL MEANS FOR ELIMINATION OF CERTAIN TYPES OF STRAY LIGHT IN THE SECONDARY OPTICS OF AN ICP-DRES SYSTEM. T. Schmitt. Johnson Controls, Inc., 5757 North Green Bay Ave., Milwaukee, WI 53201 and J. P. Walters, Chemistry Dept., St. Olaf College, Northfield, MN 55057.

When analyzing several different matrices on an ICP, one may encounter a situation where an element of interest is at trace levels in one sample type, and is the major constituent in another. We have several of these situations at Johnson Controls. 1) Matrix A - Trace lead in wastewater; Matrix b - trace analysis of lead and lead alloys. 2) Matrix A - Trace sulfur in lead alloys; Matrix b - trace analysis of sulfuric acid. With each situation, it is necessary to have an exit slit for the most sensitive line of the element of interest when analyzing for that element at trace levels. However, when analyzing a matrix where this element is a major constituent, this exit slit and the associated secondary optics are flooded with unwanted radiation. Very often this will cause severe stray light problems in the secondary optics of adjoining channels on the polychromator. To remedy this situation, we have installed two, stepper-motor driven shutters in front of the problem exit slits in our vacuum polychromator. The controls to these shutters are mounted externally. This allows whole or partial blocking of these exit slits at will, essentially eliminating the stray light problems. It also allows partial spatial profiling at these exit slits. Construction, installation, calibration, and use of the shutters in the apparatus will be discussed. The net effect on the background and the detection limits of the interfaced channels will also be discussed.

3 ANALYSIS OF STEEL FOR SULFUR, PHOSPHORUS AND BORON BY ICP EMISSION SPECTROMETRY USING A VACUUM MONOCHROMATOR. D.D. Nygaard, D.S. Chase, M.K. Conley, and D.A. Leighty, Instrumentation Laboratory Inc., One Burtt Road, Andover, MA 01810.

IL's Plasma-200 ICP Emission Spectrometer with a vacuum monochromator accessory is used to analyze steel for sulfur, phosphorus, and boron. Sample preparation will be discussed; spectral interferences in both the conventional UV and the vacuum UV will be itemized; and the methods of matrix matching, internal standard, and standard addition will be compared as a means to eliminate sample introduction matrix effects. All analytical procedures are verified by analysis of NBS standard reference materials.

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4 POTASSIUM HYDROXIDE/POTASSIUM SUPEROXIDE AS A FLUX FOR ICP ANALYSIS OF HAZARDOUS WASTE SAMPLES. J. Lowry, and E. Bour. Environmental Protection Agency, National Investigations and Enforcement Center, Denver Federal Center, Building 53, Denver, CO 80225. J. Rasmuson and R. Strode. Fred C. Hart Associates, Inc., Environmental Protection Agency (NEIC), Denver Federal Center, Building 53/Box 25227, Denver, CO. 80225.

Materials sampled from drums and associated areas in uncontrolled hazardous waste sites may vary from mineral matter such as contaminated soils, chemical byproducts, and various paint pigments to organic materials such as fats from tannery waste. Moreover, the samples are often complex, containing a mixture of solid, aqueous, and organic multiphases. Thus, application of a single method to all sample types, for example, as desired by the EPA Contract Laboratory Program, is difficult. Water/potassium hydroxide mixtures, which melt at under 150°C have been employed to destroy organic matter previous to drying the sample/flux mixture. Mineral matter is then effectively fused at around 550°C. After the addition of potassium superoxide, which aids in the dissolution of certain minerals, the reactions are performed in modified carbon crucibles. The flux is dissolved in nitric acid with the addition of hydrogen peroxide to facilitate dissolution of elements such as molybdenum, silicon, titanium, and tungsten. Quantitative recovery from various standard reference materials has been demonstrated for thirty elements including volatile elements such as As, Se, and Sb.

5 THE ANALYSIS OF GEOLOGICAL MATERIALS BY A SCANNING ICP SPECTROMETER. Duane S. Chase, Dr. Danton D. Nygaard, David A. Leighty, Mary J. Conley. Instrumentation Laboratory, Inc., Analytical Instrument Division, One Burtt Rd., Andover, MA 01810.

The elemental analysis of geological materials is often difficult because of the complex matrices that are common to many types of soils, ores, and rocks. A scanning ICP Spectrometer is well suited for the analysis of these materials because graphics capability, observation height optimization, and wavelength selection can elucidate the best analytical parameters for each element.

Several geological reference materials were obtained from the U.S. Geological Survey National Bureau of Standards in Canmet. These materials are typical of the types of standards that are analyzed in many laboratories. The samples were prepared by acid dissolution and lithium metaborate fusion. The acid procedure utilized nitric acid (HNO_3), perchloric acid ($HCLO_4$), and hydrofluoric acid (HF) and the fusion was carried out with a 3 to 1 flux to sample ratio. The two methods were compared for ease of preparation and metal recovery.

Complex matrices often generate a large amount of stray light which can degrade the detection limit and analytical results. Two optical systems with stray light rejection ratios of 1 to 10^3 and 1 to 10^6 were compared to determine the advantages of an optical system with a superior stray light rejection ratio.

6 DETERMINATION OF RARE EARTH ELEMENTS IN GEOLOGICAL SAMPLES. J. Mears, C. O. Ingamells, and J. Rasmuson, AMAX Extractive R&D, 5950 McIntyre Street, Golden, CO. 80403.

A Na_2O_2 sinter/oxalic acid separation procedure for determination of rare earth elements from 5 gram analytical subsamples at ppm and sub-ppm levels on a direct reading instrument with no rare earth channels will be presented. The method will be contrasted with other ICP rare earth techniques in the literature such as ion exchange. Sampling, optical, and applications considerations will also be addressed.

7 THE USE OF SODIUM PEROXIDE AS A SINTERING AGENT FOR THE ICP ANALYSIS OF DIFFICULT ELEMENTS AND MATRICES. J. Rasmuson, J. Mears, G. Fogleman, and F. Pitard, AMAX Extractive R&D, 5950 McIntyre Street, Golden, CO. 80403.

Both Na_2O_2 fusions and sinters effectively dissolve many sample types encountered in an extractive metallurgy laboratory. This presentation focuses on details of the developed methods as well as advantages and limitations for multi-element analysis by inductively-coupled plasma (ICP) spectrometry. In particular, analysis of difficult elements such as Cr, Nb, Mo, Sn, and Pb and difficult matrices such as chromite concentrates and other laterite-related materials will be explored.

8 Abstract not available.

9 LASER-ENHANCED IONIZATION SPECTROMETRY IN FLAMES. Robert B. Green, Department of Chemistry, University of Arkansas, Fayetteville, AR 72701.

Laser-enhanced ionization spectrometry (LEIS) is a new method for trace metal determination. Laser excitation enhances the ionization rate of the analyte in an atmospheric pressure flame. The laser-related current is detected with electrodes. This paper will provide an introduction to LEIS and its capabilities. Signal production and collection will be discussed along with the practical aspects of LEIS. Current work to extend LEIS to refractory metals will be reported. An C_2H_2/N_2O flame has been used with an immersed electrode. Recently, a total consumption burner has been evaluated for LEIS. This burner is attractive because of the high sample throughput and LEI's insensitivity to scattered light. In addition to furthering the analytical methodology, determinations at the pg/mL level suggest that LEIS measurements are possible in less than ideal sample environments where optical measurements have been inadequate. This research has been supported by the NSF.

10 PLASMA MASS SPECTROMETRY - A NEW ANALYTICAL TOOL. D.J. Douglas, G. Rosenblatt, E.S. Quan, SCIEX®, 55 Glen Cameron Road, Unit # 202, Thornhill, Ontario, L3T 1P2, Canada and R.G. Smith, X-Ray Assay Laboratories Ltd., 1885 Leslie St., Don Mills, Ontario, M3B 3J4, Canada

A new Inductively Coupled Plasma Mass Spectrometer (ICP/MS) system capable of rapid multi-elemental and isotopic analysis has been developed. Some of the unique features of the system, which are important for the analyst are simple spectra with very few spectral interferences, detection limits for most elements in a narrow range from 0.1 ppb to 10 ppb, and large practical dynamic range of at least 6 orders of magnitude. The ICP/MS system is also capable of performing rapid isotope ratio measurements and multi-elemental isotopic dilution determinations in a convenient manner. The importance of these features for elemental analysis will be illustrated through results obtained on both real samples and reference materials in the geological and environmental areas. The importance of this technique for geological exploration, through the use of isotope abundance measurements will also be discussed.

11 A THEORETICAL STUDY OF ATOMIC AND IONIC DISTRIBUTIONS IN AN INDUCTIVELY COUPLED PLASMA. Kuang-pang Li, University of Lowell, Lowell, MA 01854

Freedom from chemical interferences has often been claimed to be a major advantage of inductively coupled plasma (ICP) over convential flame spectrometry. However, numerous investigations have recently indicated that matrix interactions do occur in ICP. These interactions are critically dependent upon experimental conditions. A small change in the rf power, gas flow rate, or observation height may render a significant signal enhancement into a severe depression. Explanation for these observed effects has not been satisfactory.

The mechanism of chemical and physical processes in an ICP is not exactly known. The fact that most authors do not bother to specify and characterize their zones of observation further complicates our understanding of plasma matrix interactions. In this report we attempt to attack this problem through a kinetic approach. A set of rate equations for a reasonable reaction scheme are established and solved for the distribution functions of atoms and ions in the plasma. These functions are them compared with the observed spatial profiles. The correlations will be used for modification of the original scheme toward establishing a more reasonable mechanism.

12 THE ANALYSIS OF GEOLOGICAL MATRICES VIA A RAPID SCANNING HIGH RESOLUTION PLASMA EMISSION SPECTROMETER SYSTEM Wm. J. Kinsey, R. Craig Seeley, SpectraMetrics/ Beckman Instruments, Inc., 204 Andover Street, Andover, MA 01810

The determination of major, minor, and trace elements in geological samples is a mature analysis. However, obtaining accurate and precise data is usually resultant of proper sample preparation techniques incorporated with capable instrumentation. This report will cover dissolution techniques for a variety of geological matrices. Evaluation of fusions, acid dissolutions, and pressure digestions will be made. The performance of a computer-controlled, direct current plasma, rapid scanning, high resolution spectrometer will be evaluated when confronted with this application.

The availability of determining up to 60 elements for each analysis and the option of choosing from a library of 300 wavelengths along with the echelle optics, makes this instrument very attractive when working in a complex spectrum. Operating parameters and figures of merit will also be documented in this study.

13 A STUDY OF INTERFERENCES IN D.C. ARGON PLASMA EMISSION SPECTROMETRY, Joseph Sneddon and Vili A. Fuavao, Department of Chemistry, New Mexico State University, Las Cruces, New Mexico 88003.

Effect of various concentrations of alkali and alkaline earth elements on the determination of lead in waters and biological samples by DCP emission spectrometry will be described. % enhancement will vary with different elements. A method of calculating the plasma temperature will be described and results will be presented which show no significant changes in electron temperature of plasma excitation zone with increasing concentrations of alkali and alkaline earth elements. A method of reducing or minimizing this interference will be described where a large quantity of Aluminium and Lithium buffer is added to all solutions. Further results in the use of the DCP for major, minor and trace metal analysis will be presented.

14 FAST SEQUENTIAL PLASMA EMISSION SPECTROSCOPY: RECENT DEVELOPMENTS, A.W. Boorn A.T. Zander, T. Karlinski, R. Bosshart, Beckman Instruments, Inc., 75 Foundation Avenue, Ward Hill, Haverhill, MA 01830

The advent of computer-controlled slew scanning spectrometers has greatly increased the use of plasma emission spectroscopy as the general technique of choice in multi-element analysis. The ability to select any group of wavelengths, for any elements amenable to determination by plasma emission, is only achieved in a reliable and cost-effective manner if certain stringent instrumental requirements are met. Specifically, a highly accurate and reproducible opto-mechanical system for positioning the grating is necessary. The instrument used in this work achieves ±0.0005nm dynamic wavelength accuracy over extended time periods, without either recalibrating the wavelength drive or 'searching' for the analyte peak. High analytical throughput (determinations/minute) must be maintained for cost-effective operation. Twenty different wavelengths minute are readily measured with a mean rsd of about 3.5% and detection limits within a factor of 4-5 of those obtained with longer (2-3 second) integration times. High resolution is mandatory in plasma emission spectroscopy. A 0.75M echelle grating spectrometer is a key feature of this instrument and provides resolution of better than 0.005nm. Finally, the software operating the system involves menu-selection and virtually no typing on the keyboard. The above listed features will be illustrated by analytical results for various NBS SRM's.

15 THE APPLICATION OF EMULSIFIERS TO ORGANIC/AQUEOUS MATRICES FOR DCP ANALYSES. R. R. Comtois, Wm. J. Kinsey, SpectraMetrics, Incorporated, 204 Andover Street, Andover, MA 01810.

Aqueous and organic matrices are currently analyzed via various spectrochemical methods. Atomic emission and absorption spectroscopy methods that generate a fine mist from a liquid sample often require a dilution step during the preparatory stage. This presents few problems with aqueous matrices as the availability of high purity water and inorganic reagents is excellent. However, when confronted with analyzing various organic matrices the dilution subject can become a problem. Obtaining high purity cutting agent that is miscible can be difficult. Possibly the dilution is warranted so as to modify the background or viscosity among a variety of organic matrix samples. In this case, a single dilutent is unachievable and a mixture of solvents is requisite.

The goal of this investigation was to determine the feasability of adapting emulsifiers as matrix modifiers/dilution agents. In this application, the aqueous/organic mixture was run as a fine suspension. The DCP was chosen as the source for this study due to its ruggedness while handling complex samples. Data includes figures of merit, shelf-life, sensitivity and optimum operating parameters for the determination of trace constituents in various organic samples.

16 OIL ANALYSIS VIA A NEW AUTOMATIC INJECTION AND DILUTION SYSTEM (AIDS) FOR ICP EMISSION SPECTROMETERS S.J. Evans and R.J. Klueppel, Baird Corporation, 125 Middlesex Turnpike, Bedford, MA. 01730

ICP emission spectroscopy is an effective technique for the simultaneous measurement of trace and additive metals and metalloids in crudes and lubricating fluids. Analytical procedures for ICP have traditionally required that samples undergo a preparation step, normally dilution into an organic solvent, prior to analysis. This chemical pretreatment 1) limits real sample throughput to approximately 15 samples per hour and 2) necessitates special training of technicians working with organic chemicals and 3) suffers from particulate settling, a problem with prediluted samples. Our work has been directed towards total automation of oil analysis by ICP through the implementation of the AIDS device. This automatic injection and dilution system allows the delivery of a uniform and highly reproducible diluted sample to the plasma. Since dilution is automatic and coincident with sample uptake, throughput rates of 80 samples per hour, each analyzed for up to 60 elements, can be routinely achieved. This report details the construction of the device and discusses its analytical performance on used lubricating oils. Effects of varying viscosity oils will be examined. While this presentation relates to oil based systems, potential applications to a wide range of sample types will be outlined.

17 THE REDUCTION OF INTERFERENCES IN GRAPHITE FURNACE ATOMIC ABSORPTION. M. A. CUNLIFFE and D. E. Shrader, Varian Instrument Group, AA Resource Center, 205 W. Touhy Ave., Park Ridge, IL 60068.

Interferences in graphite furnace AAS may be classified as chemical, those which affect the population of analyte atoms, or spectral interferences that arise as a result of overlap of the non-specific absorption signal with the analyte absorption peak. Over the past few years, much research has been conducted to determine ways of reducing or eliminating these interferences in furnace AA.

Two techniques developed have been those of chemical modification of the sample and the use of graphite platforms in the furnace. Chemical modification of the sample can reduce many chemical interferences and is the most straightforward means of reducing non-specific (background) absorptions. With platforms, the higher temperatures experienced by both analyte and matrix in the vapor phase can lead to reduced chemical and background interferences. The use of one or both techniques provides a very powerful analytical tool for the reduction of furnace interferences.

Recent studies involving the use of chemical modification and/or graphite platforms with Varian's GTA-95 graphite tube atomizer will be discussed. Complex matrices such as seawater, biological fluids, and petroleum products were studied. Recommendations on the use of chemical modifications or platforms along with accuracy data and calibration requirements will be presented.

18 NEW ATOMIC ABSORPTION BACKGROUND CORRECTION TECHNIQUE. S. B. Smith, Jr., R. G. Schleicher, Mary J. Conley, Instrumentation Laboratory, Inc., Analytical Instrument Division, One Burtt Rd., Andover, MA 01810. G. M. Heiftje, Indiana University, Dept. of Chemistry, Bloomington, IN 47405.

It is also possible to use a single source for background correction. This eliminates source alignment and imaging problems, thereby improving analytical accuracy. Until recently, single background correction could only be accomplished by utilizing the Zeeman effect, this paper will describe a new technique which requires only a single HCL source, and does not require atomization cell modification. The technique can be applied to all elements and to both the flame and furnace atomization techniques.

The principle utilizes the phenomenon that as the hollow cathode lamp current HCLi is increased, the spectral emission line becomes broader and experiences self-reversal. The self-reversal is due to atomic absorption within hollow cathode lamp envelope and the broader spectral line is due to effects as collosional and/or pressure broadening at higher energy inputs. By comparing the absorbance of an atomic cell at relatively low HCLi and the absorbance at relatively high HCLi, it is possible to separate the specific absorbance and the non-specific absorbance thus yielding a simple, one HCL source, background correction system that is useful throughout the analytical spectrum. A system that does not depend on other external lamps or accessories.

Analytical examples demonstrating the application of this new technique will be presented.

19 GRAPHITE TUBE ATOMIZER PERFORMANCE-ASTM GRAPHITE FURNACE ROUND ROBIN FOR FURNACE. M. A. Cunliffe, L. M. Voth, and D. E. Shrader, Varian Instrument Group, AA Resource Center, 205 W. Touhy Ave., Park Ridge, IL 60068.

Analysts over the past decade have increasingly used graphite furnace atomizers to allow them to determine metals in the µg/L and sub-µg/L range. Federal and state regulatory agencies, i.e. the EPA, have approved furnace methods for many metals. However, furnace techniques are not troublefree and may require matrix modification of the sample and/or calibration by the method of standard additions.

Recently, ASTM ran a graphite furnace round robin for fourteen metals in water samples. The purpose of this round robin was to determine whether graphite furnace techniques could be included as standard methods by ASTM. Numerous labs participated including Varian's AA Resource Center. The instrumentation utilized was the Varian AA-975 spectrophotometer, GTA-95 graphite tube atomizer, and PSD-95 programmable sample dispenser. Concentrations for the unknowns and a quality control check sample were determined for both distilled and drinking water.

Optimum parameters, necessary matrix modifiers, and performance for the fourteen elements will be presented. Data and results from the ASTM graphite furnace round robin unknowns and QC sample will be shown. Determined concentrations will be compared to true values and mean values of the labs participating. Discussion of these results will be included.

20 DETERMINATION OF SELENIUM IN HORSE BLOOD BY HYDRIDE GENERATED FLAME ATOMIC ABSORPTION SPECTROPHOTOMETRY, Joseph Sneddon and Britt L. Porter, Department of Chemistry, New Mexico State University, Las Cruces, New Mexico 88003.

The development of a hydride generated flame atomic absorption method for the determination of selenium in horse blood will be described. Blood samples are digested in a mixture of nitric and perchloric acids. Standards are made from a selenium based drug, MYSOLE™-E, specially developed for horses suspected of suffering from selenium deficiency. The selenium is generated by a solution of sodium borohydride and swept by nitrogen to an air-acetylene flame for analysis. Several experimental factors including, flame conditions, concentration of hydrochloric acid, volume etc., were optimized for maximum performance fo the system. The analytical performance characteristics of this method will presented as will the results of a field trial involving several horses in the West Texas/Southern New Mexico area.

21 ISOTOPE DETERMINATIONS BY ATOMIC ABSORPTION SPECTROSCOPY: THEORY AND SIMULATION, K.A.S. Pathiratne and Raymond J. Lovett, Department of Chemistry, North Dakota State University, Fargo, ND 58105.

The ability to distinguish between isotopes using atomic absorption spectroscopy depends on the hyperfine splitting of the level, the isotope shift, the spectral line broadening, and the specific isotopic level and the total concentration of the element. The factors which influence isotopic discrimination will be quantified using a computer simulation of the absorption system. A discussion of which elements are amenable to isotope analysis will be presented. Special attention will be paid to Cu, Pd, and Ga, elements with known hyperfine structure.

22 DETERMINATION OF METALS IN COMPLEX MATRICES BY FORMING VOLATILE METAL CHLORIDES, R.W. Chong and R.K. Skogerboe, Department of Chemistry, Colorado State University, Fort Collins, CO 80523.

The separation of an analyte from its sample matrix without the use of reagents would save time and possible contamination. The formation of volatile metal chlorides is one way of achieving this. A system has been built where HCl gas interacts with a sample forming volatile chlorides which are then swept into the flame of an atomic absorption instrument. Results of various metals in blood and solid matrices will be presented.

THE COOLED HOLLOW CATHODE DISCHARGE. K. Burton and D. Mehs. Fort Lewis College, 23 Durango, CO 80301.

While most conventional hollow cathode discharge (HCD) lamps used in atomic absorption spectrometers usually do not feature cathode cooling, investigations of the physical and chemical nature of this discharge have often employed water-cooled cathodes. It has been claimed that cooling results in narrower spectral emission lines as well as stabiler lamp operation. In order to more completely understand the effects of cathodic cooling, we have studied the effect of cathode temperature on some of the spectral and plasma properties of the HCD lamp.

A demountable hollow cathode lamp fitted with a water-cooled cathode holder was used in these experiments. The temperature of the cathode holder, which is in good thermal contact with the cathode itself, was controlled by the flow of a thermostatted fluid from a circulating water bath. Various combinations of discharge current, cathode material, fill gas, and gas pressure were considered. Spectral line intensities of both resonance and non-resonance lines were determined as a function of cathode temperature. Atomic excitation temperatures as a function of cathode temperature were also obtained.

The results of these investigations have implications for the design of AAS light sources where stability of operation and narrow emission lines are desirable characteristics. Insights into the mechanisms responsible for the observed behavior lead to a more complete description of the fundamental nature of this low pressure discharge.

24 DETERMINATION OF BERYLLIUM ON FILTERS FROM AIR SAMPLING. J. L. Long, Rockwell International, Rocky Flats Plant, Energy Systems Group, P. O. Box 464, Golden, CO 80401

The determination in a graphite furnace atomic absorption spectrophotometer of beryllium (nanogram quantities) collected from an airstream flowing through a paper filter was improved significantly by extensively modifying the analytical procedure. Subsequently, the technique used for preparing "blind" standards was improved. The average standard error was reduced by a factor of six. Modifications to the sample preparation procedure were made after an investigation of the effects of acid concentration, lanthanum addition, and time for reaction. A five microliter sample was used for furnace injection. The improved procedure for preparing standards eliminated a serious loss of beryllium, which had been occurring routinely, and resulted in a large negative bias in the standard error. The most significant remaining problem is the presence of beryllium in the filter paper used for sample collection.

25 ATOMIC ABSORPTION ANALYSIS OF FINE AND COARSE AIRBORNE DUST. Stephen P. Kelty and C. J. Weschler, Bell Laboratories, Holmdel, N. J. 07733.

Simultaneous indoor and outdoor aerosol particles (dusts) were collected at two sites in the southwest United States. The samples were taken using two dichotomous air samplers which separated each indoor and outdoor sample into a fine (<2.5μm diameter) and coarse (2.5-15μm diameter) fraction. The Teflon membrane filters on which the samples were collected were extracted with nitric acid in an acid digestion bomb. The extracts were then analyzed using graphite furnace atomic absorption spectroscopy. The use of the L'vov platform, matrix modification and automated standard addition techniques for the analysis of several elements are described. It has been observed that the majority of elements are in higher concentration in one or the other of either the fine or coarse mode dust. In addition, relationships in the relative amounts of analyte in indoor, outdoor, coarse and fine dusts will be discussed. Finally a mention of the relationships between indoor and outdoor dust concentrations will be made.

26 DETERMINATION OF TRACE METALS USING ORGANIC EXTRACTION GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY, I. Yin, M. Robles, and T. M. Niemczyk, Department of Chemistry, The University of New Mexico, Albuquerque, NM 87131.

Analysis of biological materials for trace metals using atomic absorption spectroscopy is often very difficult due to the extremely low levels of the analytes and the very complex matrix. Using graphite furnace atomization can greatly increase sensitivity and lower detection limits to the point where the method appears to be useful, except for the fact that biological matrices often cause such severe interferences that the numbers lack adequate precision. Complexing the metal ions with a suitable chelate and extracting into an organic phase has proved successful for many determinations by flame atomic absorption. We will demonstrate that this technique shows considerable promise when used with the graphite furnace as well. The problems of making the organic extractions in matrices of this type, as well as problems associated with reproducibly introducing the organic phase directly to the furnace will be discussed.

27 INNOVATIVE MODIFICATIONS TO THE DELVES CUP BLOOD-LEAD ANALYSIS PROCEDURE Patricia Taylor, GM Industrial Hygiene Dept., 3-229 Res. Adm. Bldg., GM Technical Center, Warren, MI 48090

The Delves cup technique for blood-lead analysis involves the atomization of lead from a nickel cup into a ceramic tube and analysis by atomic absorption. The method is rapid and sensitive. The efficiency of the method is greatly affected by a few variables which, when controlled, have resulted in improved reproducibility and increased accuracy. The purpose of this paper is to address these variables.

28 IDENTIFICATION OF INSOLUBLE ORGANIC PARTICULATE MATERIAL FROM VEHICULAR TRAFFIC. Kent J. Voorhees and William D. Schulz, Dept. of Chemistry/Geochemistry, Colorado School of Mines, Golden, CO 80401.

Insoluble organic particulate material generated by motor vehicles in highway operation was collected and characterized by pyrolysis/GC/EIMS. Particulate Organic Material (POM) was collected with HiVol samplers in the Eisenhower Memorial Tunnel, Interstate 70, Loveland Pass, Colorado. The particulates were size sorted in four steps from less than 0.6μ to greater than 10μ by virtual impactors and also size unsorted. Concentration of POM was approximately 60 $\mu g/m^3$. POM was exhaustively extracted with a wide solubility parameter range of organic solvents. The total amount extracted over the four size range steps of <0.6μ to >10μ ranged from 27% to 47%.

Pyrolysis chromatograms of all size steps of insoluble tunnel POMs were nearly identical and very similar to the pyrolysis chromatogram of tire tread material. Over 100 compounds were detected from pyrolysis of the insoluble POM and over 80 compounds were identified. The chromatograms showed an unexpected paucity of heteroatom compounds and polynuclear aromatic compounds.

29 DEVELOPMENT OF CHROMATOGRAPHIC TECHNIQUES FOR THE ANALYSIS OF SYNFUEL SAMPLES.
A. P. Toste, T. R. Pahl* and R. B. Myers, Geosciences Research/Engineering and *Biology/Chemistry Departments, Pacific Northwest Laboratory, P. O. Box 999, Richland, WA 99352.

A variety of synfuel samples were analyzed for their organic/metallorganic and mutagenic content: oil shale retort waters, a shale oil, and coal liquefaction products. Their organic content proved to be so complex that extensive chromatographic fractionation was necessary before detailed organic analyses, GC and GC-MS, could be undertaken. C_{18}-partition chromatography was useful in extracting the mutagenic organic fraction from the retort waters. In general, the mutagenic activities of the retort waters were quite low. Normal phase HPLC, using an NH_2-column and a three-solvent mobile phase system (hexane, dichloromethane and isopropanol) yielded considerable fractionation of the organic/mutagenic species in all of the synfuel samples studied. In general, the mutagens ranged from moderately polar to polar. Further fractionation of the still-complex NH_2-HPLC fractions by reverse-phase HPLC facilitated the organic analyses considerably. Compounds ranging from hydrocarbons and polynuclear aromatic hydrocarbons to phenols and carboxylic acids have been identified. In a related study, steric-exclusion chromatography using Sephadex proved useful for fractionating organic and metallic species in the retort waters. Evidence suggests that a number of distinct metallorganic species are present in the retort waters. Prepared for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

30 DETERMINATION OF SELENIUM IN MARINE SEDIMENTS BY GAS CHROMATOGRAPHY
K.W. Michael Siu and Shier S. Berman
Division of Chemistry, National Research Council of Canada, Montreal Road, Ottawa, Ontario, Canada. K1A 0R9

Selenium concentrations in marine sediments were determined by gas chromatography with electron-capture detection. The sediments were decomposed in an acid mixture. Selenium was converted into 5-nitropiazselenol, extracted into toluene and introduced into the chromatograph. The detection limit was 0.2 pg Se injected or 20 ng Se per g sediment. The standard deviation was about 7%.

31 APPLICATION OF CAPILLARY GAS CHROMATOGRAPHY TO THE ANALYSIS OF PESTICIDE AND INDUSTRIAL CHEMICAL RESIDUES IN FOODS.
Norbert V. Fehringer and Stephen M. Walters, U.S. Food and Drug Administration, Pesticide and Industrial Chemical Research Center, 1560 E. Jefferson, Detroit, MI 48207.

Many laboratories involved in the analysis of pesticide and industrial chemical residues in foods use the retention ratio data compiled by the Food and Drug Administration in its Pesticide Analytical Manual (PAM) for the tentative identification of pesticide and industrial chemical residues detected in samples. Since these data were compiled using packed gas chromatographic columns, a study was undertaken to determine if these retention ratios could be used when applying capillary gas chromatography to residue analysis. Retention ratios of a selected group of 108 reference standards of the materials listed in the PAM tables were determined on four W.C.O.T. capillary columns. These columns were obtained from four commercial suppliers and were coated with four different methyl silicone phases. Some applications of capillary gas chromatography to the analysis of residues, including 2,3,7,8-tetrachlorodibenzo-p-dioxin, in samples will also be discussed.

32 ENERGY TRANSFER CHEMILUMINESCENCE DETECTION OF POLYCYCLIC AROMATIC AMINES IN HPLC. Kenneth W. Sigvardson and John W. Birks, Department of Chemistry and Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder, Colorado 80309.

Peroxyoxalate chemiluminescence is applied to the HPLC detection of polycyclic aromatic amines (PAA). These compounds are excited by the decomposition products of the reaction between hydrogen peroxide and bis(2,4,6-trichlorophenyl) oxalate. The reagents are introduced by post column mixing and the emission is observed with a fluorescence detector with its source turned off. The method yields linear responses of over three orders of magnitude and in many cases is more sensitive than fluorescence. Chemiluminescence detection has been found to be highly selective for PAA in complex samples such as shale and coal derived oils. In these synthetic fuels, PAA have recently been found to be among the most mutagenic constituents. Applications in the analysis of synthetic fuels will be discussed and comparisons will be made to existing state of the art methods. Finally chemiluminescence detection will be compared to conventional chromatographic detectors.

33 THE RENAISSANCE IN ANALYTICAL CHROMATOGRAPHY. Walter Jennings, University of Califonia, Davis CA 95616.

For most cases of qualitative and quantitative analysis, separation remains a critically important step; chromatography continues to offer the most powerful means of achieving separations. Recent advances in two fields..gas chromatography (GC) and (column) liquid chromatography (LC) are particularly worthy of exploration. In GC, these developments have occurred primarily in the areas of column technology and injection techniques, and have led to the general availability of rugged, dependable capillary systems. Capillary GC is no longer an exotic technique reserved to the analytical elitist; with its wider acceptance has come the realization that it can not only provide improved separations, shorter analysis times, higher senstivities, and improved quantitation, but that it is also--on any comparable basis--less expensive to purchase, install and operate; as a consequence, the rate of conversion to capillary GC has become almost exponential.

In time, we will find ourselves treading this same path in the field of LC. LC would be expected to be a more versatile (and more powerful) separation tool than GC; both the stationary phase and the mobile phase can be used to exercise selectivity; however, "catchy" acronyms notwithstanding, LC has so far failed to even approach its analytical potential. Detection has been a major limitation. For those solutes with strong properties of flourescence or uv absorption, sensitivity is often acceptable, but for most materials, our methods of detection are relatively insensitive. Hence we face a dichotomy: separations can be enhanced by using smaller diameter (or even open tubular) columns, but these impose impossible demands on the cells and methods normally available for detection. The incorporation of fiber optic waveguide technology now permits the delivery of much more energy to restricted volumes of sample, resolving this conflict and opening a whole new vista in the area of LC.

34 SELECTIVE SORPTION OF ALDEHYDES, KETONES AND ALCOHOLS BASED ON COMPLEXATION. E. J. Williams and R. E. Sievers, Dept. of Chemistry and CIRES, Univ. of Colorado, Boulder, CO 80309.

The technique of sorbent trapping is a very useful method for the determination of trace amounts of organic compounds in ambient air, and an extensive literature exists which details the use of porous polymer materials for this application. A large number of diverse compounds can be quantitated by preconcentration using sorbent traps followed by thermal desorption into a gas chromatograph. However, very volatile compounds present at trace levels in air cannot be determined with this method due to trapping inefficiency during sampling. This is because the volume of air which needs to be sampled to collect the minimum amount of a material to be detected (by flame ionization detector) exceeds the breakthrough volume for most sorbent materials. There are some materials which have been used as sorbents that retain compounds so strongly that thermal desorption results in the decomposition of the sorbate. This necessitates solvent extraction to remove the sorbed compounds, which increases analysis time and introduces possible error.

We present here a description of a modified porous polymer material which has been used to selectively and reversibly trap from air oxygenated compounds, such as ketones and aldehydes. The selectivity is achieved by coordination of nucleophilic species to a europium(III) ion which has been immobilized on the polymer. Synthesis of the selective sorbent was accomplished by introduction of a β-diketone moiety on the surface of a styrene-divinylbenzene co-polymer, followed by incorporation of Eu(III). The synthesis and characterization of the polymer and some examples of its usefulness are presented.

35 SIMULTANEOUS QUANTITATIVE ANALYSIS USING DUAL CAPILLARY COLUMNS OF DIFFERENT POLARITIES. Cherylyn W. Wright, Biology and Chemistry Department, Pacific Northwest Laboratory, P. O. Box 999, Richland, WA 99352.

Complex organic matrices, such as coal liquefaction and shale oil products and by-products, may be comprised of hundreds or thousands of individual components. State-of-the-art high resolution gas chromatography does not generally provide sufficient separation to allow accurate quantitation of many compounds of interest. Quantitation of individual components is often important in health effects related analyses since different compounds vary in mutagenic or carcinogenic potency. Although more selective and isomer-specific stationary phases are being developed, such phases are not yet readily available. The concept of dual column capillary chromatography has been applied which combines the different resolving characteristics of two capillary columns coated with different stationary phases. In this approach, both columns are connected either to a single injection port or in tandem. Analysis of complex mixtures in this fashion produces complex chromatograms, but the information obtained provides a means of obtaining quantitative data for individual components not resolved on any one column. In addition, peak-to-peak comparisons can provide an internal quantitative check. Quantitative applications to a shale oil process water and various coal liquids chromatographed on stationary phases of the SE-54 and Superox-type will be presented. Work supported by the U.S. Department of Energy under Contract No. DE-AC06-76RLO-1830.

36 NMR STUDIES OF CHROMATOGRAPHIC SURFACES, R. K. Gilpin, IBM Instruments, Inc. Orchard Park, P.O. Box 332, Danbury, CT 06810, M. E. Gangoda, Kent State Univ., Kent, Ohio, 44240.

In liquid chromatography the most commonly employed stationary phases generally are synthesized via mono- and tri-reactive silanes. In the past, models of such surfaces have ranged from static to dynamic in nature. Likewise, these same models typically have been developed from only chromatographic measurements or from results obtained from experiments carried out under conditions which little resemble chromatographic parameters.

Although conventional ^{13}C FTNMR has been used widely to investigate molecular dynamics, its application to study chromatographic materials has been limited. Such limitations are due to problems of signal intensity and resonance width arrising from low coverage and abundance, and hindered molecular mobility respectively. These drawbacks may be overcome by selectively enrichment of individual methylene units resulting in a single resonance. Thus, such labeled NMR experiments in combination with appropriate chromatographic measurements have provided a better understanding of surface dynamics.

37 HPLC OF NOBLE-METAL-8-HYDROXYQUINOLINATES. B. Wenclawiak; and F. Bickmann. WWU Anorg. Chem. Inst. Analyt. Abtlg., Corrensstraße 36, 44 Münster, W-Germany.

Most of the well known chelating agents react with a number of metal-ions. In photometric trace analysis there are often interferences due to the several metal chelates present. High pressure liquid chromatography can be used to separate and determine each individual metal-chelate, but a suitable system of chelate-phase-eluent has to be found.

We have examined the liquid chromatographic behavior of a number of noble-metal-8-hydroxyquinolinates. The chelates are prepared with a simple "melt under water" of 8-hydroxyquinoline (oxine). It is possible to separate the oxinates either on reversed-phase with- or on normal-phase without water in the eluent. The sample preparation before injecting, the detection and the composition of eluents will be discussed.

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HIGH PERFORMANCE LIQUID CHROMATOGRAPHIC MEASUREMENT OF NITRITE IN AQUEOUS SOLUTION BY IN SITU FORMATION OF METHYL NITRITE. Norman E. Skelly, The Dow Chemical Company, Analytical Laboratories, 574 Building, Midland, MI 48640; Antonius C. Oomens, Ferdinand G. Schuurhuis, The Dow Chemical Company, Terneuzen, The Netherlands

Nitrite is found in a wide variety of natural systems. It also has found extensive use as a food preservative and corrosion inhibitor, and for the prevention of bacterial growth in coolant formulations for metal cutting. Methods for its measurement range from the classic colorimetric spectrophotometric approach to the more esoteric instrumental techniques. It was observed that when an aqueous nitrite solution was injected onto a reversed-phase high performance liquid chromatographic column in an acidic methanol-water mobile phase, it was held longer than expected if the species, nitrous acid, was being retained by ion suppression. Analogous retention was found when ethanol or isopropanol were substituted for methanol. It was concluded that methyl nitrite was being formed in situ when methanol was present in mobile phase. Similarly, ethyl and isopropyl nitrites would be present if ethanol or isopropanol were the mobile phases, respectively. Data will be presented to support this. Based on this methodology, chromatograms will be shown illustrating the determination of nitrite in aqueous solution, a germicidal aerosol, and a herbicide. It was also found that alkyl nitrites will undergo transesterification in the mobile phase to form the corresponding nitrite of the alcohol used in the mobile phase. Peak height and peak area for injected nitrite were found to be linear over a concentration range of 0.1 to 1000 ppm. Sensitivity based on three times signal-to-noise was .05 ppm, for a 20-µl injection and 0.002 absorbance units full scale.

39 THE ESTIMATION OF PHYSICO-CHEMICAL PROPERTIES BY GC/LC TECHNIQUES. Raymond C. Crippen, Crippen Labs., INC., Consulting and Research Chemist, 4027 New Castle Ave., New Castle, DE 19720

Gas and liquid chromatographic techniques are used to estimate physico-chemical properties of a variety of chemical compounds.

Compounds at the beginning of a homologous series can be expected to deviate from the bulk of the homologs. However, deviations in physical properties in the straight line portion of the curve can predict more accurate values using GC/LC techniques. A number of these deviations are noted in the literature and more accurate values can be predicted using these techniques.

40 FLUOROCARBON POLYMER DERIVATIVES AS HPLC PACKINGS. Richard W. Siergiej and Neil D. Danielson, Dept. of Chemistry, Miami University, Oxford, OH 45056

Phenyl Kel-F is prepared by reacting Kel-F 6061 (100% polychlorotrifluoroethylene) and phenyllithium in THF under helium. From IR and elemental analysis data, substitution of the chlorine in the polymer for phenyl groups is the primary reaction occurring. Various chromatographic parameters such as the reduced plate height, sample capacity, column porosity and permiability indicate phenyl Kel-F is pelicular in nature. Based on selectivity data, the retention mechanism is found to be solvopholic in nature. The retention order of various functionalized benzenes is identical to that found for C-18 silica. Applications of phenyl Kel-F for the separation of mixtures containing N-alkyl anilines and aromatic hydrocarbons will be demonstrated. Ion-exchange HPLC packings are prepared by the functionalization of phenyl Kel-F. A strong cation exchanger is produced by sulfonation of phenyl Kel-F. A strong anion exchanger is made by chloromethylation of phenyl Kel-F followed by the addition of triethylamine to form a quaternary ammonium group. The ion-exchange capacity is 0.20 meq/gm for the cation exchanger and 0.16 meq/gm for the anion exchanger. The effect of pH, ionic strength and mobile phase counter ion on solute retention are examined in order to demonstrate the ion-exchange mechanism. Reverse phase properties are also shown to be present with both ion-exchange packings. Separations of neutral and charged organic solutes as well as inorganic ions will be presented.

41 DATING OF NINETEENTH CENTURY NAVAJO TEXTILES VIA THE HPLC IDENTIFICATION OF RED PIGMENTS. A. L. Hedlund, J. B. Wheat, Henderson Museum, R. E. Sievers, Dept. of Chemistry and CIRES, Univ. of Colorado, Boulder, CO 80309, K. C. Brooks, Dept. of Chemistry, Univ. of Colorado, Denver, CO 80202.

The Navajo Indians had no good native source of red dyes for textiles. They had to rely on trade as a source of red dyed fabrics. Fabrics can be dated by comparing the dye used with information on documented textiles of known time period. Wheat and Wenger have determined that the two predominant dyes were cochineal and lac. Both are insect dyes and contain substituted anthraquinones as the major pigments.

Fabric samples are extracted with sulfuric acid and analysed by HPLC. A reversed phase, C-18, column is used with water/acetic acid/acetonitrile as eluent. UV-VIS detection and stopped flow spectra provided sensitive identification of the red pigments present in milligram sized fabric samples.

42 DECONVOLUTION OF MULTICOMPONENT LIQUID CHROMATOGRAPHIC PEAKS USING COMPLETE EXCITATION-EMISSION FLUORESCENCE SPECTRA. D. E. Seizinger. U.S. Department of Energy, Bartlesville Energy Technology Center, P.O. Box 1398, Bartlesville, OK 74005.

Current fluorescence detection of co-eluting species in chromatographically separated peaks which are mixtures of polycyclic aromatic hydrocarbons (PAH) has not been successful. The detection techniques included selective wavelength monitoring and stop-flow scanning. However, a new fluorescence scanning technique called excitation-emission spectra (EEM) allows potential detection of multicomponent mixtures in a single liquid chromatographic peak. The EEM technique involves microprocessor or computer control of the excitation (EX) and emission (EM) wavelength drives. Either the EX or EM wavelength is programmed for repetitive scanning while the nonscanning wavelength drive is increased a programmed wavelength increment. The stored spectral data are plotted in either contour or isometric (3D) format. Analysis of these plots can show the presence of several species with different EX and EM spectral characteristics which co-eluted from the chromatographic column. Application of the EEM scanning technique to chromatographic separation of complex mixtures of PAH extracted from diesel particulate samples will be shown.

43 APPLICATIONS FOR CHROMATOGRAPHY IN THE SEMICONDUCTOR INDUSTRY, J. A. Fulton and H. M. Gordon, Western Electric Company, P. O. Box 900, Princeton, NJ 08540.

The electronics industry is rapidly moving towards as wide a use as possible of plastic packages for Very Large Scale Integrated Circuit (VLSI) devices. To avoid high failure rates of the final product, it becomes necessary to characterize the polymers used not only as single materials at room temperature, but at elevated temperatures and in contact with other materials. Methods have been developed using a variety of sampling and preparation techniques in conjunction with gas chromatography and gas chromatography/mass spectrometry for characterization of various polymers used in providing protective films and package encapsulation. Examples of the methodology used, results obtained and the implications of these results will be discussed for select polymers, such as novolac epoxies and room temperature vulcanized silicones. These examples will include use of pyrolysis and headspace as sampling techniques and the use of chemical derivatization for quantitation.

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44 PREPARATION OF A PRIMARY NATURAL GAS STANDARD FOR CALORIFIC AND SPECIFIC GRAVITY CALCULATION FROM GAS CHROMATOGRAPH ANALYSIS Richard E. Stern Colorado Intrstate Gas P. O. Box 276 Pueblo, Colorado 81002

This work presents a simple procedure using two component mixtures and physical testing to verify the contents of a four component primary standard (nitrogen, methane, ethane, propane). Higher molecular weight constituents present in natural gas are quantitatively determined by use of relative response factors (E. F. Barry, D. M. Rosie Journal of Chromatographic Science 59 (1971) Page 269). Relative error is shown to be ± 1 BTU and ±.003 in specific gravity which is within the precision of the physical testing instruments. Observations in calibrating process chromatographs for custody transfer applications show a need for programming the microprocessor to calculate response factors from the published relative response data instead of depending on a multicomponent blend.Credit is given to John Light, retired chemist, in instituting this procedure at the Devine laboratory, Pueblo, Colorado.

45 FUTURE APPLICATIONS OF COMPUTERS IN R&D, Keith J. Caserta, The Procter & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45247

This paper will discuss those applications of computers in research and development which go beyond the tasks of instrumental control, monitoring, and data presentation that we have come to expect from our intelligent laboratory devices. These emerging technologies include robots for sample preparation and analysis, image analysis for quantitation of visual information and robotic vision, electronic mail and archiving, data base management for tracking project status, corporate information, and personal files, and artificial intelligence for capturing expertise, enhancing the creative process, and processing complex problems of human perception. Example applications of these technologies to R&D problems will be discussed, along with innovations likely to occur in the next few years to facilitate the broader use of these advanced computer techniques. Existing applications of laboratory robots, low cost, high performance image analysis devices, small, portable computers, and multiple-computer systems, all developed in P&G laboratories, will be presented.

46 LANGUAGES, OPERATING SYSTEMS AND NETWORKS. Raymond E. Dessy, Chemistry Department, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061.

As chemists begin to use intelligent instruments and personal computers in teaching and research it is essential that they have an appreciation of the factors which can affect the efficiency of these devices. Like their human operators, computers are constrained by the communication skills they possess. It is difficult, or impossible, to articulate concepts, or implement functions, for which we do not have the proper vocabulary. It is essential that we be organized, and communicate and coordinate with others. In the computer world these comprise the elements of languages, operating systems and networks. This presentation will focus on the vocabularies and philosophies of these important areas. Fourth generation languages such as FORTH and ADA will be discussed with a view toward the constructs desirable in a laboratory language. Laboratory operating systems will be reviewed. Finally, baseband, broadband and token rings will be surveyed as conduits for local area networks.

47 A MICROCOMPUTER NETWORK FOR THE SMALL INDUSTRIAL-CLINICAL-ANALYTICAL LABORATORY. Jeffery J. Brosemer and Daniel J. Macero, Department of Chemistry, Syracuse University, Syracuse, New York 13210.

At our laboratory, we are designing and implementing a laboratory microcomputer network which is based upon the family of operating systems developed by Digital Research (Pacific Grove, CA): CP/M, MP/M and CP/NET. The network permits distributed operation for greater user reliability and maximization of computer peripherals, e.g., printer, plotter, and/or high density disk storage. A Z80-B microprocessor with a 6 MHz clock serves as the network master controller for dynamically allocating resources to satellite laboratory microcomputer-based requestors on a first come, first served basis. Slaves competing for a network device, can request and obtain exclusive use of the device to carry out a given task; after completion of the task, the device is once again made available for use by the other network users. The microcomputer network can handle up to 16 users, is interrupt driven, and also permits a degree of background/foreground operation.

48 THE USE OF COLOR GRAPHICS AS AN ANALYTICAL TOOL IN THE LABORATORY, P. V. Passalacqua, PERKIN-ELMER Corp., Norwalk, CT 06856

Color graphics is an important tool in the analytical laboratory which literally adds a new dimension to various types of displays and plots. Although color is used in many different ways, most implementations can be categorized as either highlighting or color coding. In regard to highlighting, it is an extremely effective method to call attention to a portion of an alphanumeric screen, and, furthermore, unlike blinking and inverse video attributes, it can be used for hard copy as well. Another widespread use of color graphics for analytical applications involves color coding mechanisms. Color coding ranges from simple identification schemes, i.e., sample status or sample lot, to a complex use of color to depict the solvent composition in gradient liquid chromatography. Other important uses are seen when overlaying multiple spectra, resolving overlapped peaks and determining integration limits. Dramatic effects will be discussed which result from instantaneous color swapping due to changing a color bit-map. Also, specific examples of the use of color graphics on the recently introduced PERKIN-ELMER Model 7500 Laboratory Company will be presented for inductively coupled plasma spectroscopy, infra-red spectroscopy and liquid chromatography applications.

49 COMPUTER MODELING OF CHROMATOGRAPHIC CURVES PRODUCED BY AN ON-COLUMN REACTION, Arthur J. Boyer, T. William Gilbert, Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221

A photochromic azo dye, 1-(4-ethoxyphenyl)-2-(4-methoxynaphthyl)-diazene, was found to undergo geometrical cis-trans isomerization around the azo group within the HPLC time frame. A mathematical model of chromatography based on reaction-diffusion-convection theory (C. DeLisi, et al, J. Chromatogr., 240(1982), 283) was altered to include the isomerization phenomenon and was adapted to the FORTRAN language by substituting the discrete approximation for the continuous differential equation. A subprogram based on the Lochmuller-Sumner skewing model (C. Lochmuller, and M. Sumner, J. Chromatogr. Sci., 18(April 1980), 159) allowed tailing of computed data to be achieved. The experimental chromatogram and the modeled chromatogram were plotted on the same coordinates. Overlap of these data sets was made to occur by adjustment of the parameter system describing the modeled chromatogram. Good agreement was found between a direct assay utilizing HPLC and computer modeling the first-order rate constant for the on-column cis-to-trans conversion of this dye at 50° C in methanol.

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50 A MICROCOMPUTER CONTROLLED AUTOMATIC TITRATION SYSTEM, A. L. Lewis, D. R. Trammell, Exxon Nuclear Idaho Co., Inc., P. O. Box 2800, CPP-602B, Idaho Falls, Idaho 83401

A microcomputer controlled automatic titration system consisting of a precision buret, an electrometer, an analog to digital converter and a Hewlett-Packard 85 or 87 microcomputer will be described. The unit is in routine daily use in a service analysis laboratory. The advantages of this system over commercially available titration systems are many. It can be easily tailored to nearly any fixed endpoint or automatic endpoint titration. It provides specific instructions to the analyst for a given titration, provides him with hardcopy output, and can send the titration results directly to a larger lab management computer. The system is capable of results with precision better than 0.02%. The automatic operation of the titrator frees the analyst to do other work while the titration is proceeding. Instrument control, data acquisition, and data processing are done using assembly language programs and the IEEE-488 bus of the HP-85.

51 THE INTERACTION OF NETWORKING, SAMPLE INFORMATION MANAGEMENT AND CHROMATOGRAPHIC ANALYSIS, David Beggs, Doug Greig, Jeff Justice and Edward Long, Nelson Analytical, Inc., 10061 Bubb Road, Cupertino, CA 95014

With the advent of improved methods, techniques and instrumentation, more and more information is becoming available to the analytical chemist at ever increasing rates. In order to effectively handle this influx of data and information, the chemist must find efficient methods of data reduction and analysis. The low-cost microcomputer provides an excellent means of accomplishing this. The microcomputer system including appropriate software and peripherals can provide instrument control, data acquisition and data reduction capabilities in an automated mode. Also, the microcomputer can collect, store, retrieve and sort auxiliary sample information. By using appropriate interfaces, the microcomputer can transmit all or part of this information to other locations across the room or around the world. This paper will provide a description of the microcomputer in the chromatography laboratory. Specific emphasis will be placed on the capabilities of the microcomputer to collect, reduce, collate and transmit data and information.

52 TRANSFORM DATA PROCESSING TECHNIQUES APPLIED TO CROSS-CORRELATION CHROMATOGRAPHY. Scott R. Frazer and Michael F. Burke, Department of Chemistry, University of Arizona Tucson, Arizona, 85721.

Computerization of chromatographic instrumentation has allowed the design and implementation of experiments in chromatography which utilize data processing and transform techniques to enhance S/N, resolution, or both. In addition, computer control of the sampling system allows variable and multiple inputs into what is generally considered to be a single input system. Combining these two processes, these data processing abilities can be applied to a multiple input experiment, usually after a Fourier transform operation has converted the data to its frequency domain. Cross-correlation is then used to extract usable information. Thus, after cross-correlating an input profile with its subsequent output, one can apodize, truncate, or even run a second cross-correlation on the resultant spectrum before reconverting to the time domain. Chromatography offers a straightforward way to optimize cross-correlation parameters as the experiment can be made as simple or complex as one wishes to make it without having to simulate data. Frequency Modulated Correlation Chromatography was used to study both multiple injection and data processing parameters. The dependence of multiple injection parameters such as extent of modulation, injection rate, and data acquisition rate on the retention time and variance of the chromatographic peaks has been considered. The form and point of truncation, cross-correlation with reference spectra, and other methods to increase resolution without excessive side lobe introduction have also been investigated.

PROCESSING CHROMATOGRAPHIC DATA USING A PERSONAL COMPUTER

Daniel Klopp, Hewlett-Packard Co., Rt. 41, Avondale, PA 19311

Interpreting instrumental analytical data has historically been the task of the laboratory chemist. Only the largest laboratories have been able to afford computers and software to aid in this task. This is now changing with increased proliferation and sophistication of inexpensive personal computers. This paper describes use of a HP85A Personal Computer interfaced to a HP5880A Gas Chromatograph through a serial data communications link. Several applications in which the personal computer was used to solve a specific analytical problem will be discussed. Among these are a routine for peak identification using retention indexing, calculation of hydrocarbon type on naphtha samples, and application of computer graphics for sample identification and comparision.

54 A MICROPROCESSOR-BASED DATA SYSTEM FOR CONTINUOUS FLOW ANALYZERS, Craig B. Ranger, Lachat Instrument Division, 10500 N. Port Washington Road, Mequon, WI 53092

The Lachat QuikChem Data System was designed specifically to interface with continuous flow analyzers of both the unsegmented and segmented flow type. Most notably these include Lachat QuikChem Automated Chemistry Systems and the Technicon AutoAnalyzer. The primary applications reside in performing the requisite control, data reduction and reporting functions. A host of special programs is also available to accommodate various customer requirements and the user can optionally write, compile and execute his own programs written in FORTRAN. Furthermore, the CP/M operating system is provided standard so the user can run any of the hundreds of CP/M-based programs which are widely available. For example, accounting or word processing software can be run directly on the system with no additional hardware.

The Data System is designed in a master/slave configuration. The mast computer mediates primary user interface functions, stores operation programs, performs editing functions, archives data files, prints laboratory reports and plots calibration curves. The slave computer interfaces between the master computer and the analytical system. Its functions are to control and coordinate the various analyzer modules and to collect, condition, digitally convert and transmit detector signals to the host for processing.

Standard software consists of the CP/M operating system, run-time package, screen-oriented editor and plotting routine. FORTRAN and custom software are optionally available.

55 COMPUTER APPLICATIONS IN PETROLEUM RESOURCE APPRAISAL. R. A. Crovelli. U. S. Geological Survey, P.O. Box 25046, Denver Federal Center, Denver, Colorado 80226

Applications of the computer to oil and gas resource appraisal include computer-graphics routines. The following numerical examples are given from several projects of the U.S. Geological Survey. Petroleum finding rates are described by computer-produced decline curves. Petroleum play analysis is based upon a Monte Carlo simulation technique. Computer-generated probability curves are used to estimate the quantity of undiscovered, recoverable crude oil, associated-dissolved gas, and nonassociated gas in an assessment area or sedimentary basin. Computer aggregation methods are used to assess the petroleum potential in two or more basins.

56 MICROCOMPUTER-BASED ELECTRONIC HANDBOOK OF CHEMICAL INSTRUMENTATION. F. A. Settle, Jr Virginia Military Institute, Lexington, VA 24450 and M. A. Pleva, Washington and Lee University, Lexington, Virginia 24450.

An electronic information system available on Radio Shack Model III computers has been developed by the Scientific Instrumentation Information Network and Curricula Project (SIINC)*. Information modules have been developed for gas chromatography and gas chromatography mass spectrometry and are available on small floppy diskettes. Uni on atomic absorption spectroscopy and liquid chromatography will soon be available.

The microcomputer allows the system user to control easily the mode of presentation of text, diagrams, and sample data. An RS-232 interface and a telephone modem permits the user to load the most current information directly from the master files located on a larger Burroughs main frame computer at VMI to his diskettes.

In addition to the above features, users with specific needs may create their own files for purposes of training personnel, recording methods, etc. The system provides rapid access to current information on chemical instrumentation and, thus, becomes a dynamic reference work.

*National Science Foundation Grant, SED 79-19780

57 UTILIZATION OF A DATA BASE MANAGEMENT SYSTEM IN THE UNDERGRADUATE INSTRUMENTAL METHODS OF ANALYSIS LABORATORY. Robert J. Merrer, Department of Chemistry, Western Connecticut University, Danbury, Connecticut 06810

The Perkin-Elmer Laboratory Information Management System (LIMS/2001 has been integrated into the Instrumental Methods of Analysis Laboratory course at Western Connecticut State University. Information management systems involve some of the most complex software in existence. A laboratory data base management system essentially enables entrance and extraction of information from a file in varying combinations without nee for extensive programming each time a new format is required. In this specific case, utilization involves a selective search of previously stored sets of data and merges them with a high level language to create a specific format and to perform calculations. Also, the student assembles, accesses, and searches his own set of data. Specific steps will be shown to configure a data base. Coulometric titration with biamperometric endpoint and atomic absorption examples will be given. These will show the system functioning as an "electronic" or automated laboratory notebook.

58 SPATIALLY AND CHEMICALLY MODIFIED ELECTRODES, Royce W. Murray, P. Burgmayer, P. Pickup, C.R. Leidner, Kenan Laboratories of Chemistry, University of North Carolina, Chapel Hill, NC 27514

Coatings on electrodes of polymeric films containing electroactive groupings are interesting because new chemistry is often involving in making the polymer or film, because the electron conductivity of the solvent/electrolyte wetted film involves novel electron transfer chemistry, because the films can act as electron transfer mediator-catalysts, and because the polymeric films can be used to tailor the electrode surfaces both chemically and in space. Illustrative examples will include new forms of spatial tailoring dubbed sandwich electrodes and ion gates electrodes.

59 **SURFACE-MODIFIED CdS PHOTOCHEMICAL DIODES: WATER CLEAVAGE REACTION,** A. J. Frank and Kenji Honda, Solar Energy Research Institute, 1617 Cole Boulevard, Golden, CO 80401.

Single crytals of CdS coated with electrically conductive polypyrrole films and overlaid with catalysts on opposite faces have been studied with respect to the visible light-induced water-splitting reaction. The conductivity and hydrophobicity of the modified surfaces, the amount and composition of the catalyst loading, the nature of the electrolyte, and the pH and ionic strength of the solution affect the stability and catalytic activity of CdS. Nearly all the photogenerated holes can be directed to O_2 production with no photocorrosion of the semiconductor detectable.

60 **MODIFICATION OF ELECTRODE SURFACES WITH POLYMER BOUND TRANSITION METAL PHOSPHINE COMPLEXES.** Daniel L. DuBois, Photoconversion Research Branch, Solar Energy Research Institue, 1617 Cole Boulevard, Golden, CO 80401.

Methacrylamide polymers with pendant monodentate (poly-P_1), bidentate (poly-P_2), and tridentate (poly-P_3) phosphine ligands have been prepared. The polymers react with various transition metal complexes to produce polymers with pendant transition metal phosphine complexes. For example, reaction of two equivalents of poly-P_2 with $Ni(COD)_3$ (COD = 1,5-cyclooctadiene) produces $Ni(poly\text{-}P_2)_2$ and reaction of $Mo(N_2)_2(PPh_2Me)_4$ with one equivalent of poly-P_3 produces $Mo(N_2)_2(poly\text{-}P_3)PPh_2Me$. THF solution of these polymers can be used to modify various electrodes. The electrochemistry of the surface bound complexes will be discussed and compared with that of their solution analogues.

61 Electrochemical (and Other) Investigations of the Ion Exchange Selectivities and Transport Properties of Various Ion-Containing Polymers. J. A. Ferguson, M. N. Szentirmay, N. E. Prieto and C. R. Martin, Dept. of Chemistry, Texas A. & M. University.

The ion-containing polymer (ionomer) Nafion (1) has proved to be a useful membrane material for a wide variety of electrochemical processes (2). Because of this versatility, a number of reports describing transport properties of Nafion films have appeared. Surprisingly, however, a thorough investigation of Nafion's ion-exchange selectivity has yet to appear; this is surprising because all applications of Nafion rely on its ability to act as an ion exchange material. We have used chemically modified electrodes based on Nafion films to obtain ion exchange selectivity coefficients for a variety of electroactive counterions. These studies have shown that ion exchange reactions in this ionomer are driven primarily by the hydrophobic effect. We have also studied ion exchange selectivity using fluorescence probe experiments, and these studies have produced analogous results. Results of both sets of experiments will be reported. The analytical utility of this rather unusual selectivity data will be discussed.

Nafion is a cation exchange ionomer. Ionomers similar to Nafion but containing fixed quaternary ammonium sites (i.e., anion exchange ionomers) have also been prepared (3). The solubility, transport and ion exchange characteristics of these potentially useful ionomers have not been studied. Solvent swelling studies have allowed us to determine procedures for obtaining solutions of these ionomers from which films may be cast. We have used such solutions to prepare chemically modified electrodes based on these anion exchange polymers.

62 ELECTRON SHUTTLING BY ADDED REDOX COUPLES TO ENHANCE ELECTROCATALYTIC RATES AT ELECTRODES COATED WITH NAFION FILMS. Daniel A. Buttry and Fred C. Anson, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125.

A method is presented for the incorporation of water-insoluble metal-free porphyrins into Nafion films on graphite electrodes. Subsequent metallation of the incorporated porphyrin is demonstrated for the case of tetraphenylporphyrin and cobalt(II). The resulting Nafion coating is an effective catalyst for the electro-reduction of dioxygen to hydrogen peroxide. Slow diffusion of the CoTPP within the coating limits the reduction currents to small values. However, when $Ru(NH_3)_6^{3+}$, a complex with a comparatively large diffusion coefficient in Nafion, is also incorporated into the coating the dioxygen reduction currents are dramatically increased because the ruthenium complex serves to shuttle electrons rapidly between the electrode surface and the metalloporphyrin catalyst.

63 THICK-NAFION-FILM MODIFIED ELECTRODES. C. Michael Elliott and J.G. Redepenning, Department of Chemistry, Colorado State University, Fort Collins, CO 80523.

Thick films of insoluble bulk Nafion can be brought into intimate electrochemical contact with mercury. Electroactive cationic species such as methyl viologen (MV^{+2}) can be exchanged into the Nafion either prior to mounting the film or from the electrochemical solution. MV^{2+} in these films has been studied under a variety of solvent and electrolyte conditions by cyclic voltammetry and chronocoulometry. Thick-Nafion-film modified electrodes possess certain advantages, both theoretical and practical, over modified electrodes prepared from solubilized Nafion. First, their insolubility allows their use in most non-aqueous systems. Second, the dense structure and thickness of the polymer allows for theoretical treatments that are less ambiguous than in the case of electrodes prepared from solubilized Nafion. This work is supported by U.S. Department of Energy (DE-AC02-80ER10589).

64 Luminescence Probe of Polymer Morphology in Thin Electrode Films. Marcin Majda, Department of Chemistry, University of California, Berkeley, CA 94720.

The electrochemical behavior of $Ru(bpy)_3^{3+/2+}$ couple was studied in thin films of sulfonated polystyrene (PSS) at Pt electrodes in acetonitrile. Cyclic voltammetry in a ruthenium-free, 0.01M $TBABF_4$ solution indicates the presence of two forms of the ruthenium couple which differ in $E^{o'}$ values by 195 mV. Based on this and related electrochemical results, morphological changes of the polymer matrix are postulated. Progressively with the oxidation of the ruthenium centers, poorly solvated domains of Ru(III) centers locked within PSS strands are being formed. Steady state luminescence from $^3[Ru(bpy)_3^{2+}]^*$ immobilized in a PSS film was monitored during the electrooxidation of the ruthenium centers. Sharp decay of the luminescence in such experiments is due to the quenching of luminescence by Ru(III) centers. The formation of the hydrophobic domains lowers the efficiency of the quenching process. After the extent of the oxidation exceeds 20%, the luminescence intensity increases despite contiued oxidation process. The luminescence vs. time curves were used to probe morphological changes of polymeric matrices induced by the electrochemical reactions within these polymer films in acetonitrile and aqueous solutions. Water insoluble PSS films were made by locking PSS in a crosslinked matrix of polyacrylamide. The luminescence behavior of the ruthenium complex in the PSS films of various degree of crosslinking will be reported.

65 ELECTROCHEMISTRY AND ELECTRON SPIN RESONANCE OF TETRACYANOQUINODIMETHANE MODIFIED ELECTRODES. James Q. Chambers, György Inzelt and Roger W. Day, Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600.

Tetracyanoquinodimethane (TCNQ) modified electrodes, adsorbed thin films of $(TCNQ)_x$ oligomers on platinum substrates, have been studied by voltammetric, spectroelectrochemical, and electron spin resonance techniques. In contact with aqueous electrolytes the electron acceptor sites in these films are reduced to mixtures of the radical anion, $TCNQ^{\bullet-}$, the dimer radical anion, $TCNQ_2^{\bullet-}$, the dimer dianion, $TCNQ_2^{2-}$, and the dianion, $TCNQ^{2-}$. Electrolyte effects on the reduction process and the stability of the reduced films were studied. Both monovalent and divalent ions exhibited nernstian potential dependence, and in the presence of Ca^{2+} ions the dianion state was stabilized. A maximum in the e.s.r. signal, interpreted as arising from the $TCNQ_2^{\bullet-}$ mixed-valence species, occurs at potentials in the region of the foot of the first reduction wave. The correspondence between the calculated fractional distribution coefficients, the potential dependence of the e.s.r. signal, and the absorption bands due to the radical anion and dimer dianion species has been used to extract the electrodimerization parameters from the results. Slow electrochemical steps revealed by the e.s.r. experiments are attributed to unfavorable dimerization kinetics on reduction, and isolation of unpaired electron sites in the bulk of the film upon oxidation. (Work supported by the U. S. Army Research Office.)

66 THICK-POLYMER-FILM MODIFIED ELECTRODES - POTENTIAL ELECTROCHROMIC APPLICATIONS OF RING SUBSTITUTED BIPYRIDINE METAL COMPLEXES, C. Michael Elliott and J.G. Redepenning, Department of Chemistry, Colorado State University, Fort Collins, CO 80523.

One of the potentially promising applications of modified electrodes is in the development of various electrochromic devices, for example, multicolored displays. A number of practical problems, however, are inherent in the development of devices that rely on faradaic processes. First, for many compounds only a small number of oxidation states (two or possibly three) is generally accessible. In addition it is necessary for the extinction coefficients of the chromophore to be large and for the electroactive material to be stable in each of the oxidation states.

We have prepared and studied RuL_3^{+n} complexes where L = ester substituted 2,2'-bipyridine. These complexes, in aprotic solution, can exist in as many as eight stable formal oxidation states (+3 to -4). Additionally, in each oxidation state the complex has a distinctly different color. By modification of the ligand ring substitution it is possible to prepare monomer complexes which can be coated on several electrode substrates (carbon, SnO_2, etc.) and thermally polymerized. Thick polymer films of these materials on transparent SnO_2 electrodes are electroactive and very robust. The films are strongly colored and the colors change dramatically in each different oxidation state. This work is supported by U.S. Department of Energy (DE-AC02-80ER10589).

67 RECENT DEVELOPMENTS IN PHTHALOCYANINE-ELECTRODE PHOTOELECTROCHEMISTRY. Neal R. Armstrong, Dept. of Chemistry, University of Arizona, Tucson, AZ 85721.

Recent studies of the photoelectrochemical reactions of phthalocyanine thin film electrodes will be described -- including our elucidation of the factors that lead to improved efficiencies of light to electrochemical energy conversion using these materials. It has been possible recently to increase the long-range ordering of phthalocyanines deposited by sublimation, lowering the defect density in these films and increasing the quantum efficiency of several light-assisted redox reactions to between 5% and 10%. We have been able to generate sizable photopotentials using a variety of redox couples, and to catalyze multiple electron transfer reactions such as photoassisted hydrogen evolution through the addition of transition metals to the phthalocyanine surface. The power conversion efficiencies are considerably lower than have been seen on inorganic single crystal photoelectrodes, nevertheless these results give encouragement for the further development of organometallic, thin-film photoelectrochemical devices.

68 METAL AND METAL OXIDE DISPERSED PARTICLES FOR ELECTROCATALYLYSIS. Jerzy Zak, Shaojun Dong, Wen-Hong Kao, Duane Weisshaar and Theodore Kuwana. Department of Chemistry, The Ohio State University, Columbus, OH 43210.

Metal and metal oxide particles dispersed directly onto or in a polymeric matrix adhering on a graphitic or glassy carbon electrode surface can serve as potent catalysts for a variety of charge transfer reactions. In general the metal oxide particles have been utilized for catalyzing organic redox reactions, which in many cases, undergo reversible charge-transfer. The extent of adsorption on these dispersed particle electrodes has been evaluated by a method introduced by Soriaga and Hubbard, i.e., successive filling/coulometry with a thin-layer cell. The metallic particles have been effective for the catalysis of reactions involving small molecules such as the generation of hydrogen or reduction of oxygen. The discussion will include a) methods of preparing dispersed particle electrodes; b) the size and distribution of the particles, c) the scope in terms of the types of substances catalyzed; d) the effect of the particles with respect to effective surface area and double layer capacitance; and e) mechanistic aspects of the catalysis.

69 THE DIRECT AMPEROMETRIC DETECTION OF CARBOHYDRATES AND AMINO ACIDS AT A PLATINUM ELECTRODE APPLIED TO LIQUID CHROMATOGRAPHY. D.C. Johnson, S. Hughes and J.A. Pe[illegible] Department of Chemistry, Iowa State University, Ames, Iowa 50011.

Molecules of carbohydrates and amino acids adsorbed on the surface of a Pt electrode in alkaline media are anodically detected by a reaction which is electrocatalyzed by PtOH formed during the initial stage of the anodic generation of an oxide layer on the electrode surface. The electrocatalytically active state of Pt is transient, however, and the analytical current rapidly decays for amperometry at constant applied potentia The sequential processes of oxide reduction, analyte adsorption and anodic detection can be managed for analytical applications by a triple-step potential waveform execute at a frequency of ca. 1 Hz. The detection system is easily applied for liquid chromatography. Detection limits are at the ppm-level and rel. std. dev. is approximately 3 % at 100 ppm. Chromatographic results will be shown for numerous samples.

70 Abstract not available.

71 STERIC EFFECTS IN ELECTRON TRANSFER REACTIONS OF TRANSITION METAL COMPLEXES. I. SYNTHESIS AND HOMOGENEOUS REACTIVITY OF STERICALLY-HINDERED REDOX SERIES. Carl A. Koval, Dept of Chemistry, Univ. of Colorado, Boulder, CO 80309

Electron transfer reactions involving transition metal complexes are usually assumed to be adiabatic, i.e. donor-acceptor orbital overlap within the precursor complex is sufficient for a smooth transition from reactants to products. We have synthesized several series of complexes in which the ligand stuctures are modified to cause steric interactions without altering the coordination of the ligand to the metal ion. The ligands include amines, pyridines, 1,10-phenanthrolines, and tripeptides. The metal redox couples include Fe^{3+2+}, Ru^{3+2+}, Co^{3+2+}, and Cu^{3+2+}.

Rate constants for all of the possible homogeneous electron transfer reactions between the members of the redox series have been measured using a Durrum stopped-flow spectrophotometer that has been interfaced to a MINC-11 minicomputer. Trends in this data will be compared to the predictions of Marcus' theory.

72 II. KINETICS OF THE REDUCTION OF $CO(III)(ALKYLAMINE)_5(X)$ COMPLEXES AT MERCURY AND PLATINUM ELECTRODES. Michael E. Ketterer and Carl A. Koval, Dept. of Chemistry, Univ. of Colorado, Boulder, CO 80309

In the early 1960's, studies of homogeneous electron transfer reactions between $Co(III)(NH_3)_5(X)$ complexes and various reducing agents led to the distinction between outer- and inner-sphere reaction pathways. Recently, Weaver investigated the heterogenous reduction of these same Co(III) complexes and related Cr(III) complexes. He was able to develop criteria for distinguishing between outer- and inner-sphere electroreductions. In order to investigate the effect of ligand size and shape on the redox reactvity of transition metal complexes, we have examined the electrochemistry of a series of $Co(III)(alkylamine)_5(X)$ complexes. The amines used were ammonia, methylamine, propylamine, and isobutylamine and X was water or chloride ion.

The rates for the irreversible reductions of the Co(III) complexes were measured polarographically and at platinum electrodes using rotating disk voltammmetry in aqueous solutions containing KPF_6 as a supporting electrolyte. Extension of the measured Tafel plots allows the electrochemical rate constants to be compared with rate constants for the homogeneous reduction of the Co(III) complexes with $Fe(II)(H_2O)_6^{2+}$. Trends in the electrochemical data for the chloro-complexes can also be compared to the rates of aquation.

73

III. HETEROGENEOUS ELECTRON TRANSFER KINETICS OF CO(III,II), FE(III,II) AND RU(III,II) COMPLEXES UTILIZING SQUARE WAVE VOLTAMMETRY.
Cindy M. Reidsema and Carl A. Koval. Department of Chemistry, University of Colorado, Boulder, CO 80309.

Many complex ion redox couples display reversible or quasireversible electrode kinetics; however, if these same complex ions are located within a hydrophobic protein structure the resulting metallo-enzymes are usually electroinactive. In order to study these steric effects, we have synthesized several series of complexes derived from pyridine and 1,10-phenanthroline ligands. The nitrogen heterocycles have been modified to contain saturated, yet water-soluble substituents. The complexes are based on $Ru(II)(NH_3)_5$(pyridine) and the tris(1,10)phenanthroline complexes of Co(II) and Fe(II).

The heterogeneous kinetics for these complexes were studied in water at platinum and glassy carbon electrodes using a relatively new technique - cyclic square wave voltammetry.

74 ELECTROCHEMICAL IN SITU MONITORING OF GROUNDWATER PARAMETERS. John A. Lanning, Univ. of Colorado at Denver, 1100 14th Street, Denver, CO 80202

An electrochemical probe has been developed for the in situ monitoring of pH, E_{Pt}, and temperature in groundwater systems. The in situ probe is self contained, field portable, and capable of operating at depths to 250 feet and in wells as small as 2 inches ID. The probe relies on commercially available, replaceable electrochemical sensors for ease in field maintenance.

The in situ electrochemical probe is designed to complement existing groundwater monitoring methods and to address the difficult task of obtaining reliable field data which are representative of a large groundwater system. The in situ measurement technique allows monitoring wells to be profiled by depth and increases measurement accuracy by not exposing samples to surface temperatures and atmospheric oxygen.

The design and operation of the in situ electrochemical probe will be discussed and results, including comparison to surface analysis techniques, will be presented.

75 ADVANCES IN ION CHROMATOGRAPHY IN THE AREA OF ENVIRONMENTAL SCIENCES. A.W. Fitchett, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94086

Over the last several years, Ion Chromatography has expanded to include all types of ionic components in all types of matrices and application areas. This paper will highlight the advances that have been made in the area of environmental analysis and will include air and water applications. The ability to determine inorganic anions (F^-, Cl^-, NO_3^-, SO_4^{2-}, CN^-, S^{2-}, etc.) metals (Na^+, K^+, Ca^{2+}, Mg^{2-}, $Fe^{2+/3+}$, Pb^{2+}, Cd^{2+}, Zn^{2+}, etc.), organic acids, sequestering agents (EDTA, NTA), and phosphorous species (ortho, pyro, tripoly) will be shown. The status of IC within EPA, ASTM, and Standard Methods will be discussed.

76 NEW DEVELOPMENTS IN NBS ENVIRONMENTAL AND BIOLOGICAL STANDARD REFERENCE MATERIALS CERTIFIED FOR TRACE CONSTITUENTS. Robert Alvarez, Office of Standard Reference Materials, National Bureau of Standards, Washington, DC 20234.

NBS issues over 900 homogeneous materials certified for chemical composition and/or physical properties. A number of these Standard Reference Materials (SRMs) are certified for constituents, at trace levels, classified by EPA as priority pollutants. The SRMs are issued to assist investigators in calibrating instrumentation, determining the accuracy of methods, and validating experimental data. SRM 1639, Halocarbons (in methanol) for water analysis, provides certified concentrations of seven volatile organic compounds: chloroform, carbon tetrachloride, trichloroethylene, dichlorobromomethane, tetrachloroethylene, chlorobromomethane and bromoform. Each certified concentration, at the ng/μL(mg/L) level, is based on the analytical results of gas chromatography and the concentration calculated from the mass of the halocarbon added to a known mass of the methanol. This new SRM should have three main applications: identifying halocarbons in samples, calibrating instruments, and adding accurate amounts of known halocarbons to samples. These are the same types of applications for which SRM 1647, certified for polynuclear aromatic hydrocarbons, is used. Details of the certification of these and other SRMs under development, such as urine and human serum, will be discussed.

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77 SILVER IN THE MARINE ENVIRONMENT: A PRELIMINARY BUDGET FOR PUGET SOUND. N. S. Bloom and E. C. Crecelius. Battelle Marine Research Laboratory, 439 W. Sequim Bay Road, Sequim, Washington 98382.

Methods have recently been developed at Battelle for the precise and accurate determination of silver in all types of marine environmental samples (water, sediment, tissues, and air particulates) at ambient levels. For seawater, a 100-fold preconcentration technique using coprecipitation with Cobalt (II) - APDC, followed by graphite furnace Zeeman atomic absorption (GFZAA) has given a detection limit of 0.1 Ng/L Ag. All other types of samples are digested with HNO_3 or HNO_3 + H_2SO_4, and diluted by a factor of 1:100. Analysis of the digestate by the same technique (GFZAA) leads to typical detection limits of 0.002 µg/g dry weight basis. Studies on Puget Sound using these techniques have revealed several interesting facts, including the following: (1) silver is the most enriched metal in the sediments, showing an enrichment factor of about 10, compared to 5 for lead and mercury; (2) most silver input into the sound comes from sewage discharges, and is rapidly transported to the sediment; (3) silver is extremely bioconcentrated in sediment-dwelling creatures such as clams and crabs (i.e., 10^6 times water concentration). (The Marine Research Laboratory is part of the Pacific Northwest Laboratory, which is operated for the Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.)

78 ACCIDENTAL AND INCIDENTAL HONEYBEE POISONING BY PESTICIDES. T. D. Spittler, J. B. Bourke and R. A. Morse. New York State Agricultural Experiment Station, Cornell University, Geneva, NY 14456.

*Honeybees, the primary insect pollinator for agricultural crops, have been subject*ed to increased depredation by pesticides. Poisonings of foraging bees occur as a result of both legal applications and misuse of agricultural chemicals. In 1980, 140 bee and pollen samples collected at the sites of suspected chemical bee kills in New York State were analyzed for methyl parathion and carbaryl, the two materials most frequently responsible for bee kills. Fifty samples contained lethal levels of methyl parathion and fifteen contained lethal levels of carbaryl, five samples fell into both categories. One-third of the methyl parathion containing samples were analyzed for azinphos-methyl; *two samples were found to contain high levels of this material. Therefore, chemicals* initially suspected of being responsible for specific bee kills because of their recent application in the vicinity frequently were vindicated in light of other chemical residues shown to be present.

79 THE DEVELOPMENT OF A CONCEPTUAL LANDSCAPE MODEL TO ASSESS THE EFFECTS OF ACIDIC DEPOSITION ON DRINKING WATER SUPPLIES
J.C. Méranger[1] and T.H. Khan[1] and David Gladwell[2], Ray Lett[2] and C. Succi (Vairo)[2], National Health and Welfare, Ottawa, Ontario K1A OL2[1], Barringer Magenta Ltd., Rexdale, Ontario M9W 5G2[2], Canada

It is acknowledged that acidic deposition can have adverse effects on the quality of drinking water by altering the bioavailability of trace elements. Recent studies show that acidic untreated cottage water supplies can have a corrosive effect on the water distribution system. In certain cases untreated water in prolonged contact with the cottage plumbing system can reach levels exceeding the maximum acceptable recommended by the 1978 Canadian Drinking Water Guidelines. Therefore care should be exercised when consuming water without pH control from areas which are subjected to high acidic precipitation. As a result of these observations further studies are underway to develop a conceptual model which would be used to predict the effect of acid rain on the quality of drinking water. Preliminary results will be presented on the development of a conceptual landscape acid precipitation model which will be used to determine the effects of acid deposition. Some data will also be presented on the interpretation of water geochemical data and the influence of acid precipitation of the hydrogeological regime.

80 CHEMICAL ANALYSIS OF DEW AND FROST COLLECTED NEAR DENVER, COLORADO. LeRoy J. Schroder, Michael M. Reddy, and Amy B. Good. U.S. Geological Survey, P.O. Box 25046, Mail Stop 407, Denver Federal Center, Denver, Colorado 80225.

Precipitation water quality generally is determined by chemical analysis of either a wetfall (rain or snow or both) only, or a bulk (wetfall plus dryfall) sample. Contributions to precipitation loading from sources other than rain and snow (dew, frost, and dryfall) are uncertain and may be significant in urban environments. Dew and frost collected near Denver, Colorado have been analyzed for inorganic constituents to supplement rain and snow loading data. Sampling on a plastic surface 15 centimeters above the ground began in October, 1982. Sampling at additional sites, including a control site located near the Continental Divide, was begun in February, 1983. Initial samples at all sites were analyzed for 22 chemical parameters including pH (range, 5.8 to 6.9) and specific conductance (range, 22 to 250 microsiemens per centimeter at 25° celsius. Dominant cations were calcium and sodium; chloride and sulfate were dominant anions. Barium, iron, lead, manganese, silica, strontium, and zinc concentrations were always equal to or greater than the detection limit for the analytical method used (inductively-coupled plasma, atomic-emission spectroscopy). A fog sample collected on November 10, 1982, had a pH of 4.3, specific conductance of 120 microsiemens per centimeter, and a lead concentration of 280 micrograms per liter.

81 CHEMICAL ANALYSIS OF SEDIMENT COATINGS USING SELECTIVE CHEMICAL EXTRACTION AND INDUCTIVELY COUPLED ARGON PLASMA. Briant A. Kimball, U.S. Geological Survey, Water Resources Division, Denver Federal Center, Lakewood, CO.

Concentrations of 18 elements were determined in two size fractions of stream sediment samples collected in the Uinta basin of northeastern Utah and the Piceance basin of northwestern Colorado. To evaluate the baseline chemistry of sediment coatings, the samples were sequentially treated with extractant solutions to remove selected coatings. Each solution was then analyzed using inductively coupled argon plasma (ICP). Standards for the ICP were prepared in the extractant solutions to minimize the matrix effects and to account for the interelement effects. About 4 percent of the iron, less than 1 percent of the aluminum, and 57 percent of the manganese present in the sediments were in coatings. Coatings on the sediment seemed to come off in two stages. First, there was an easily extractable part removed by sodium pyrophosphate and mild acetic acid. Next, there was a more crystalline part removed by hydroxylamine hydrochloride and ammonium oxalate. The remaining sediment was digested by hydrofluoric acid to determine the concentrations of the elements in the residue. Results were evaluated using an analysis of variance. For most elements, less than 10 percent of the total variance was due to the analytical techniques. Almost no variance was due to differences among replicate samples collected in the field. Most of the variance was due to sediment size and to environmental factors, such as differences in the geology and hydrology among the sampling sites.

82 ATOMIC ABSORPTION SPECTROMETRY FOR DETERMINATION OF TRACE METALS IN ORGANIC ENVIRONMENTAL MATERIAL AFTER DIFFERENT SAMPLE PRETREATMENTS. E. Scheubeck, H. Kunze, M. Pickel, L. Fischer, L. Schon, Siemens Corp., Research Laboratories, D-8520 Erlangen, FRG.

Atomic absorption spectrometry has proven to be an efficient analytical tool for the determinaton of trace metals. But, trace analysis of organic substances is often complicated by interferences from the organic sample matrix. So a pretreatment of the samples, appropriate for the subsequent analytical procedure, is necessary. Diverse digestion processes, such as wet and dry decomposition in open and closed vessels, were tested. Using the new decomposition device BIOKLAV (R) very low losses of readily volatile metals and very low blanks were observed. This was because all steps including drying, burning in oxygen at elevated pressure, and the absorption of the gaseous burning products were carried out in a closed pressure vessel. Weighed samples up to 30 g, e.g. wood, leaves, vegetables, oils, fat, and so on, were processed in less than 30 minutes. Trace elements to be determined were solubilized in the decomposition solution consisting of the condensed water and the burning products from the sample. In this solution trace metals from the starting substance are determined, e.g. 1-5 µg of lead and cadmium by flame or graphite tube atomization, 1-5 µg of mercury and arsenic resp. 0.1 µg of selenium by cold vapor and hydride technique. Recoveries were better than 80%.

83 A PNEUMATIC BOTTOM SEDIMENT TRAP FOR LIMNIC WATERS. George H. Setlock, Applications Technology Group, Rockwell International, Golden, Colorado 80401

A bottom sediment trap apparatus featuring remote, air-activated deployment and replicate sampling capabilities has been constructed for assessing sedimentation rates in linmic waters. The device is comprised of a "lunar-lander" tripod framework which supports an array of eight cylindrical sediment vessels. The cylinders radiate at one meter lengths from the framework's locus in a planar, rosette pattern. During sampling, each vessel's orifice is one meter above the sediment/water interface; each tube is 102 mm in diameter with a height/diameter ratio of 4.0 to promote consistent trapping efficiencies. All parts of the apparatus are either aluminum, stainless steel or PVC to maximize structural rigidity and corrosion resistance while minimizing total weight. At approximately 57 kilograms this apparatus provides a stable platform for extended periods (6-12 months) of particulate collection. An independent closure cover, consisting of a hinged lid driven by an air spring assembly, insures isolation of each sediment vessel during deployment and retrieval of the sediment trap. The air springs are connected in series and are reliably activated from the surface of the water body using a small gas cylinder. Preliminary pond sedimentation data acquired with vessel prototypes agree well with Pb-210 determined accretion rates on adjacent sediment core samples verifying the capabiity of this sediment trap design to accurately measure vertical fluxes of particle matter.

84 CADMIUM SPECIATION IN NATURAL WATERS AND THEIR EFFECT ON RAINBOW TROUT, W.C. Gorma Jr. and R.K. Skogerboe, Department of Chemistry Colorado State University, Fort Collins, Colorado 80523. P.W. Davies, Colorado Division of Wildlife, 313 West Prospect, Fort Collins, Colorado 80522.

Most water quality criteria for metals are based solely on the total metal concentrations. However, recent evidence has shown that toxicity is not related to the tot metal but is related to the concentrations of the free metal and labile metal complexe

In this paper, DPASV was used to monitor the rate of formation of cadmium-ligand complexes in tap and well water. pH titrations were employed to estimate the stabil constants of the various cadmium complexes from which the form of the complexes can b tentatively identified. Also, the toxicity of the different cadmium species on rainb trout will be examined.

85 AB INITIO ANALYSIS OF HAZARDOUS WASTE AND ENVIRONMENTAL EXTRACTS. Donald F. Gurka,[1] Michael Hiatt[2] and Richard Titus,[3] U.S. Environmental Protection Agency, Quality Assurance Division[1], Region 9[2], Las Vegas, Nevada 89109. University of Nevada at Las Vegas,[3] Chemistry Dept., Las Vegas, Nevada 89109.

Complex hazardous waste and environmental extracts have been analyzed by fused silica capillary column gas chromatography Fourier transform infrared spectrometry (FSCC/GC/FT-IR) and fused silica capillary column gas chromatography mass spectrometry (FSCC/GC/MS). The effect of co-elution, extract interferences and search library on the "total" analysis of complex extracts by combined GC/FT-IR, GC/MS was evaluated. Selected extract components were quantified by GC/FT-IR and the results compated to GC/MS quantification values. The minimum identifiable quantities of some typical environmental contaminants by FSCC/GC/FT-IR, under routine monitoring conditions, were determined. The prospects for the "total" analysis of volatile components in complex extracts by combined FT-IR, MS is discussed.

86 UNIQUE APPLICATIONS OF LASER-INDUCED FLUORESCENCE TO ENVIRONMENTAL ANALYSIS.
Stan M. Klainer, ST&E Technical Services, Inc., 20 Belinda Ct., San Ramon, CA 94583, Tomas Hirschfeld and Fred P. Milanovich, Lawrence Livermore National Laboratory, Livermore CA 94550.

Environmental monitoring procedures must be specific, sensitive and economical if they are to be acceptable to both the regulatory agencies and the organizations which must implement and use them. Given a laboratory with the best analytical equipment and competent analysts, specificity and sensitivity can be attained for collected samples provided that sample integrity is not lost during collection and transportation and provided that no cost limitation is put on the analyses. Analyzing collected samples, however, is a labor intensive process and the cost of running even a few samples can be prohibitive. There is a solution to this problem - automatic remote in-situ analysis using remote fiber fluorimetry and optrodes. The analytical method is laser-induced fluorescence which gives the desired sensitivity. The optrode, a chemical system and/or a mechanical device at the distal end of a fiber optic, furnishes the needed specificity. The ability to make up to fifty (50) unattended in-situ measurements, using a reasonably priced centralized fluorimeter system connected to the sampling sites by inexpensive optical fibers, results in acceptable economy. Physical measurements such as pressure, temperature and liquid level have been made. Chemical detection and quantification of the actinides, sulfate, inorganic and organic chloride, tracers, iron, pH and Eh are possible.

87 THEORETICAL APPLICATIONS OF MULTIPLE COMPARTMENT PASSIVE MONITORS
Neil H. Price, UBTL, 520 Wakara Way, Salt Lake City, Utah 84108

Until recently, commercially available passive monitors have typically employed only a single sampling compartment design or designs in which two separate sampling compartments have been placed in tandem one behind the other. With the tandem configuration, the analyte being collected must pass through the primary (first) sampling compartment prior to reaching the secondary (second) sampling compartment. Currently, at least one manufacturer is offering passive monitors with multiple sampling compartments arranged in a side-by-side configuration rather than in the tandem design. With the side-by-side configuration, the multiple sampling compartments can sample independently as separate passive monitors. The side-by-side configuration makes many useful applications theoretically possible. This paper describes the following theoretical applications of the side-by-side configuration multiple sampling compartment passive monitor to the field of industrial hygiene monitoring: 1) development of a passive monitor in which the monitor-indicated concentration is relatively independent of the exposure interval, when used within its functional limitations, 2) development of a passive monitor in which the monitor-indicated concentration can be corrected for effects of interferring substances, 3) development of a passive monitor which can determine the concentrations of individual components of complex mixtures, and 4) development of a passive monitor with a functional backup section design.

88 VALIDATION STUDY FOR THE FUSED SILICA GC-ATMOSPHERIC PRESSURE IONIZATION-MS METHOD FOR THE ISOMER SPECIFIC DETERMINATION OF 2,3,7,8-TCDD IN ENVIRONMENTAL SAMPLES,
W.A. Korfmacher, G.F. Moler, R.K. Mitchum, National Center for Toxicological Research, Jefferson, Arkansas 72079.

There has been an increasing interest in the isomer-specific determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) at the parts-per-trillion (ppt = pg/g) level in various types of environmental samples. Several methodologies have been developed to perform this analysis. The method developed by our laboratory includes a multistep HPLC cleanup followed by quantitation via fused silica GC-Atmospheric Pressure Ionization (API)-MS and has been described recently (Mitchum, R.K., Korfmacher, W.A., Moler, G.F., Stalling, D.L., Anal. Chem., 1982, 54, 719-722).

Our lab has been involved in a major validation study of this GC-API-MS method for the determination of 2,3,7,8-TCDD in environmental samples. This ten part validation study includes both interlab and intralab portions. The sample matrices included in this study are: fish tissue, hog fat, clay soil and water. The results of this study will validate both the cleanup and GC-API-MS method for the determination of 2,3,7,8-TCDD and will demonstrate the detection limits that can be expected from the fused silica GC-API-MS method.

89 EFFECTS OF AFTERTREATMENT DEVICES ON THE PHYSICAL, CHEMICAL, AND BIOLOGICAL CHARACTER OF DIESEL PARTICULATE. Jackson P. Scholl, Paul R. Miller, David G. Leddy, Susan T. Bagley, John H. Johnson, and Fredric J. Hibbler, Michigan Technological University, Houghton, Michigan 49931.

Modern control technology for diesel particulate emissions includes aftertreatment devices such as catalytic convertors, close-coupled catalysts, and porous ceramic filter traps (catalyzed and uncatalyzed). A multidisciplinary study on the relative effectiveness of these devices has been underway at Michigan Technological University for the past three years. The ability of each of these aftertreatment devices to change the chemical character of the organic fraction, modify the biological properties, and affect the total particulate emissions will be discussed. All studies were carried out on particulates collected from a dilution tunnel. The diesel engines were mounted on a dynomometer and operated at steady-state conditions. Samples were compared with respect to total particulate matter, sulfates, soluble organic fraction, classes of chemical species, and the Ames mutagenicity bioassay. Gas phase compositions as well as engine operating characteristics were also measured. The advantages and disadvantages of each of these aftertreatment devices will be summarized.

90 CHROMATOGRAPHIC PATTERNS IN CHARACTERIZATION OF SYNFUEL BY-PRODUCT WATERS. Damon A. Delistraty, John M. Mason, Fred G. Todd, Lynne M. Sebo and R. E. Poulson, Laramie Energy Technology Center, Laramie, WY.

In recent years many studies have presented detailed analyses of the organic solutes in synfuel by-product waters, producing a wealth of information on these materials in their raw or "as-produced" state. In the early stages of environmental control and monitoring technology development, screening techniques more detailed than organic carbon analysis, but less detailed than GC-MS, are extremely useful. Such procedures fit conceptually with EPA Level 1 and Level 2-type considerations. A combination of a gas chromatogram on a nonpolar column and a liquid chromatogram on a reversed-phase column has been used to produce a "volatility" profile and a "polarity" profile, respectively, which together form a comprehensive overview of organics in these waters. These profiles form the basis for recognition of the effect of subsequent physical/chemical/biological operations on a water. Chemical class identification becomes possible directly in some cases. Results are presented for by-product waters from processing of oil shale, coal (via underground gasification), and tar sand, surveyed for the development of this methodology.

91 CHARACTERIZATION OF WATER COMPOSITION DURING DISCHARGE FROM HYDROSTATIC TESTING OF NATURAL GAS PIPELINES. G. A. Eiceman, B. D. Baker and C. S. Leasure, Department of Chemistry, New Mexico State University, Las Cruces, New Mexico 88003.

Hydrostatic testing of natural gas pipelines is commonly practiced for testing physical integrity of new pipelines or of existing pipelines scheduled for use at increased pressure. Testing with hydrostatic pressure is accomplished by filling pipelines with water drawn from local water sources such as rivers and lakes. Then, pipelines are pressurized using air or natural gas. After these tests, lines are emptied (dewatered) using a metal or plastic plug which is pneumatically forced through the pipeline. In addition to water, unwanted deposits or residues are also removed and test waters in the U.S. Southwest are typically released into rivers directly or into stock ponds for treatment. Using high resolution gas chromatography/mass spectrometry the range of hydrocarbon content was determined as C_6 to $>C_{36}$. Present in a complex mixture of over 100 components were benzene, phenol, C_1 to C_4 alkylated benzenes and C_1 to C_4 alkylated phenols. Chemical oxygen demand was in excess of 50,000 mg/L for certain samples and concentrations of benzene and phenols were 10 to 36 mg/L and 3 to 57 mg/L respectively. Also present at concentrations >0.1 mg/L were a mixture of 8 to 10 polycyclic aromatic hydrocarbons. Influence of matrix on analytical methods, changes in composition during dewatering, and selective pre-enrichment techniques will be described.

92 COMPARATIVE STUDY OF THE ORGANIC AND INORGANIC COMPOSITION OF EL CHICHON AND MOUNT ST. HELENS ASHES. J. R. Garbarino, U.S. Geological Survey, Box 25046, MS 407, Denver Federal Center, Lakewood, Colorado 80225

Ash samples from El Chichon, Chiapas, Mexico were compared with those from Mount St. Helens, Washington, USA, with respect to the bulk ash inorganic composition and leachable inorganic and extractable organic constituents. Elemental analysis of El Chichon and Mount St. Helens ashes by X-ray fluorescence indicated that they were andesitic in composition. Leachate studies were conducted by sequentially leaching ash samples with demineralized water followed by a pH 3.5 acid solution. Leachates were analyzed for a suite of cations and anions using inductively coupled plasma emission spectroscopy, and ion chromatography, respectively. El Chichon water leachates generally contained considerably greater concentrations of major and trace cations coupled with greater sulfate and chloride concentrations. Acid leachate data indicated that El Chichon ash contained more water insoluble metal sulfates, sulfides and oxides. Characterization of organic compounds adsorbed to ash particles was based on data obtained on ash extracts analyzed by gas chromatography-mass spectrometry. El Chichon and Mount St. Helens extracts contained many of the same hydrocarbons, alcohols, fatty acids and ketones. Major differences were the presence of polynuclear aromatic hydrocarbons, dicarboxylic acids, phenolic acids and tricyclic diterpenoidal resin derivatives in the Mount St. Helens extract. Several organo-sulfur compounds were identified in the El Chichon extract.

93 A COMPREHENSIVE RADIOLOGICAL EMERGENCY SURVEILLANCE PROGRAM NEAR NUCLEAR POWER PLANTS. Joseph J. Kliment, Supervisor, Wilmington Laboratory, Division of Environmental Control, Delaware Department of Natural Resources and Environmental Control, 14 Ashley Place, Wilmington, DE 19804.

The close proximity of three nuclear power plants along the Delaware River necessitated the development of a comprehensive radiological emergency surveillance program in support of Delaware's Radiological Emergency Plan. The program consists of both continuous instrumentation and dosimetry to establish dose commitment to the population in the event of an off-site release from nuclear power faciities. The heart of the system consists of continuously operating low level Geiger-Mueller detectors strategically located at the State's air quality monitoring stations. Radiological data is continuously telemetered to a central laboratory and processed by computer to provide "real time" radiation values used in plotting plume direction and intensity for decision-making purposes. The detectors proved their worth during the Three Mile Island incident by detecting low levels of radiation at a distance of 80 miles from the plant indicating excellent detection sensitivity. A continuous radioactive iodine sampler with subsequent analysis by gamma spectroscopy is also operated adjacent to the power plant complex to establish thyroid dose levels in the event of an emergency. The monitoring program is further complimented by a thermoluminescent dosimetry network which provides an accurate account of dose exposure to the population. During a radiation emergency, trained monitoring teams utilizing portable equipment also provide field dose assessments for rapid decision-making purposes.

94 MEASUREMENTS OF THE VERTICAL FLUX AND MEAN CONCENTRATION BUDGET FOR OZONE IN A CONVECTIVE BOUNDARY LAYER, R. Pearson, Jr., *Department of Atmospheric Science, Colorado State University, Fort Collins, Colorado, 80523,* D. H. Lenschow and B. B. Stankov, *National Center for Atmospheric Research, Boulder, Colorado, 80303.*

Ozone is a key minor constituent of the troposphere - natural and polluted - and a precursor of the hydroxyl radical. Currently, attempts to improve our understanding of the budget of this molecule are active areas of research. By flying a wide-bandwidth (10 Hz) ozone detector on meteorological research aircraft equipped for turbulence measurements, it has been possible to measure the transport terms and total time derivative in a budget for the mean ozone concentration. Under appropriate conditions, the residual in this budget can be used to estimate the net production or destruction of ozone in the planetary boundary layer. After briefly reviewing the special characteristics of the instrumentation and sampling requirements, the most recent results from this experiment will be summarized.

95 TURBULENT FLUXES OF OZONE, HEAT AND MOISTURE OVER FOREST, S. R. Kawa, R. Pearson, Jr., *Department of Atmospheric Science, Colorado State University, Fort Collins, Colorado, 80523;* D. H. Lenschow and B. B. Stankov, *National Center for Atmospheric Research, Boulder, Colorado, 80303.*

Recent measurements have found large vertical fluxes and deposition velocities for ozone over coastal forests in eastern Texas. This region is noted for large areas of exceptionally flat terrain, and for the density and variety of vegetation, including extensive second and third growth forests. During June, 1982, we used an NCAR Queen Air aircraft instrumented with fast-response sensors to measure ozone, temperature, moisture and winds. Vertical profiles of ozone suggest that a concentration gradient may have existed below 200 m AGL. This would imply a very active sink near the surface, and could involve scavenging of ozone reactive hydrocarbons, as well as the expected surface deposition. The measured fluxes and deposition velocities will be presented and compared to results over other surfaces.

96 MEASUREMENT OF MEAN CONCENTRATION AND TRANSPORT OF OZONE IN SMALL CUMULI DURING CCOPE, C. J. Weaver and R. Pearson, Jr., *Department of Atmospheric Science, Colorado State University, Fort Collins, Colorado 80523.*

The essential elements in a budget for boundary layer ozone are chemical and photochemical production and destruction, and vertical transport. The transport to a surface sink is well recognized, and is actively being studied. Another possibility for transport is upward through small-scale convective elements. This latter process is poorly understood, but may be of some importance to regional air quality. In addition, if ozone is conserved on the time scale of moist convection, its measurement may provide a new tool for measuring entrainment and other processes in cloud dynamics. An NCAR Queen Air aircraft, instrumented to measure ozone and a variety of meteorological and cloud physics data, penetrated small cumuli and cumulus congestus turrets during the Cooperative Convective Precipitation Experiment (CCOPE, 1981). Preliminary results from these measurements will be given. They show that cloud liquid water does not produce a significant interference in measuring ozone, and provide information about the conservation of this gas during moist convection.

97 THE EFFECTS OF PHOTOCHEMICAL REACTIONS ON THE VERTICAL FLUXES OF O_3, NO, AND NO_x IN THE ATMOSPHERIC SURFACE LAYER: A FIELD STUDY, B. L. Woodruff, R. Pearson, Jr., *Department of Atmospheric Science, Colorado State University, Fort Collins, Color 80523;* A. C. Delany, G. J. Dolan, D. R. Fitzjarrald, D. H. Lenschow, F. L. Melchoi and A. F. Wartburg, *National Center for Atmospheric Research, Boulder, Colorado, 80303.*

The assumption of chemical flux conservation in the atmospheric surface layer may not be correct in the presence of chemical reactions. Significant flux divergence might be expected when time scales for chemical reactions and transport are the same order of magnitude. A field experiment planned for June, 1983, to measu the reaction-modified fluxes of O_3, NO, and NO_x in the surface layer will be described. The site is near the Boulder Atmospheric Observatory, about 30 km. NNW of Denver, CO., and is characterized by moderately polluted air without large local emission sources. Instruments to measure the chemical species and meteorological parameters will be installed to sample over grass. Preliminary results from one component of the experiment will be presented.

98 NITROGEN OXIDES IN URBAN ATMOSPHERES
Larry G. Anderson, Department of Chemistry, University of Colorado at Denver, Denver, Colorado 80202.

Nitrogen oxides are emitted to the atmosphere primarily as NO, with some NO_2. In the atmosphere NO is converted to NO_2 by both photochemical and thermal processes. During the day NO and NO_2 are rapidly interconverted by a series of processes which are responsible for the oxidation of hydrocarbons in the atmosphere. This paper will concentrate on the processes which are responsible for the conversion of the nitrogen oxides (NO + NO_2) to less reactive forms, and are hence important in limiting the photochemical oxidation of hydrocarbons. Principal among these is the reaction of NO_2 with the hydroxyl radical (OH) to form HNO_3. Other possible source of HNO_3 in the urban atmosphere, which may be important at night will also be discussed. In addition, the formation and decay mechanisms of PAN, NO_3 and particulate NO_3^- during both the day and night will be discussed.

99 THE EMISSION OF ORGANIC AIR POLLUTANTS FROM SHALE OIL WASTEWATERS. S.B. Hawthorne and R.E. Sievers, Dept. of Chemistry and Cooperative Inst. for Research in Environmental Sciences (CIRES), Univ. of Colorado, Boulder, CO 80309.

If shale oil is produced on a commercial scale in western Colorado, large volumes of highly contaminated wastewaters will be generated that will require control and disposal in an environmentally acceptable manner. Since most of the proposed methods of wastewater treatment and re-use involve planned or inadvertent exposure to large volumes of air, large quantities (as much as one-fourth to one-half of the dissolved organic carbon from some wastewaters) of organic solutes with high vapor pressures and low water solubilities will be emitted into the atmosphere at ambient temperatures. Raw wastewater used for cooling and codisposal with spent shale also emit a complex mixture of organic pollutants. Such emissions may require that wastewaters be extensively treated before disposal. Most of the organic species emitted during laboratory simulations of these conditions have been identified and quantitated using gas chromatographic analysis with mass spectral and flame ionization detection. Major compound classes emitted include nitrogen heterocycles, ketones, nitriles, and phenols. The analytical methodology employed and the results of these analyses will be discussed. A comparison will also be made between the results of our laboratory simulations and those of air samples collected at an operating pilot scale shale oil wastewater treatment facility.

100 THE CHANGE IN ORGANIC COMPOSITION OF OIL SHALE WASTEWATER BY TERTIARY TREATMENT TECHNIQUES. Margaret K. Conditt and Robert E. Sievers. Dept. of Chemistry and CIRES, Univ. of Colorado, Boulder, CO 80309.

The development of oil shale in western Colorado will result in chemically complex wastewaters that will require some degree of treatment. These wastewaters may be reused on-site with some treatment or may even be discharged after extensive treatment. Traditionally, wastewater discharge standards have been concerned with only gross chemical parameters such as pH, total suspended solids, total organic carbon, oil and grease, chemical oxygen demand, ammonia, and phenols. With the exception of phenol, little is known about the classes of organic compounds remaining in the wastewater to be discharged. The fractionation of an oil shale wastewater into compound classes has been used to define more extensively the organic composition of a wastewater as it is treated for disposal.

An oil shale gas condensate wastewater was evaluated by quantitating the compound classes in the water as it progressed through a wastewater treatment plant. Seventy-five percent of the dissolved organic carbon was eliminated from the wastewater after being treated by steam stripping, biological degradation and clarification. The steam stripping treatment alone reduced the hydrophobic base solutes by 60%. The nitrogen bases in this fraction were identified using a combination of mass spectral and retention time data. Quantitative analysis of the hydrophobic bases before and after steam stripping revealed that the alkylpyridine compounds were more easily steam stripped from the wastewater than aniline and quinoline compounds.

101 REMOVAL OF ORGANIC AIR POLLUTANTS BY PRECIPITATION. R. S. Hutte and R. E. Sievers, Dept. of Chemistry and CIRES, Univ. of Colorado, Boulder, CO 80309.

Precipitation, via "rainout" and "washout" is a major mechanism for the removal atmospheric pollutants. Recent research in the field has concentrated on the inorg constituents, but organic pollutants are also removed during precipitation events. Rain and snow samples collected at an urban and a rural site have been analyzed to determine the identities and concentrations of volatile and extractable organic compounds. Organic compounds in the vapor phase and in airborne particulate matter wer measured before, during and after precipitation events to determine the extent of their removal.

Organic compounds from natural and anthropogenic sources have been found in the rain and snow samples, including normal hydrocarbons, polycyclic aromatic hydrocarbo terpenes, carboxylic acids, phenols and dehydroabietic acid. Most of the organic compounds present are associated with airborne particulate matter removed by the precipitation.

102 AMBIENT NITRIC ACID MEASUREMENTS-INTERFERENCE FROM PAN AND ORGANONITROGEN COMPOUNDS Roger L. Tanner, Yin-Nan Lee, Thomas J. Kelly and Jeffrey S. Gaffney, Environmenta Chemistry Division, Brookhaven National Laboratory, Upton, NY 11973

Current measurement techniques for atmospheric levels of nitric acid are reviewed. Emphasis is placed on comparisons of data from denuder difference-integrated filter techniques and real-time, ozone-chemiluminescence techniques. Limits of detection are compared and sample transfer and artifact problems are evaluated. Difficulties in abs lute calibration of the two techniques with HNO_3 are enumerated. For most ground-sampling applications the denuder technique is superior in sensitivity and accuracy (0 ppb levels, 1-hr sampling). For airborne applications the real-time technique is superior for quantitating rapidly changing concentrations.

Interference studies reported utilize newly-modified techniques for preparing high pure peroxyacetyl nitrate (PAN), its peracyl homologs and its thermal decomposition product, methyl nitrate. Pure PAN is not retained by nylon filters but is converted t nitric oxide by molybdenum catalysts (375°C). Thus PAN does not interfere with nitric acid measurements by diffusion denuder or O_3-chemiluminescence techniques, being measured as NO_x in the latter. The differentiation of PAN from the sum of NO + NO_2 by use of ferrous sulfate is feasible, and preliminary indications are that methyl nitrate and PAN behave similarly on nylon and $FeSO_4$. The design of an instrument for differentiating NO, NO_2, PAN and nitric acid in the atmosphere is outlined.

103 HOW TO KEEP MERCURY IN THE +2 VALENCE STATE IN AQUEOUS SOLUTION. James L. Robins Environmental Protection Agency, Region VII, 25 Funston Road, Kansas City, Kansas 66115.

Mercury (Hg) in the +2 valence state is easily reduced to Hg(0) by a variety of conditions. A computer program looks at the equilibrium involved in this reduction and estimates Hg(0)/Hg total as a function of type or anion, concentration of anion, pH, and total Hg concentration. Experimental work attempts to confirm theoretical work for certain results. An evaluation is made why Hg(+2) ion in aqueous solution needs an anion such as chloride to keep from changing to Hg(0), and why an anion such as nitrate will not work as well in this capacity.

104 ELECTRON-NUCLEAR MULTIPLE RESONANCE IN PHOTOCHEMISTRY: HYPERFINE STRUCTURE OF SHORT-LIVED RADICALS

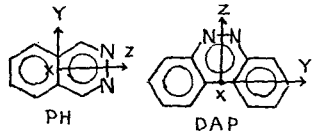
K. Möbius, Institut für Molekülphysik, Freie Universität Berlin, Arnimallee 14, D-1000 Berlin 33, West Germany

The lecture will cover our recent solution ENDOR and electron-nuclear-nuclear TRIPLE resonance experiments on primary reaction products of bacterial photosynthesis, both in vitro and in vivo, and on transient radicals in photochemical reactions of p-benzoquinone, which could be ENDOR-detected with the aid of chemically induced dynamic electron polarization effects ("CIDEP-enhanced-ENDOR"). After briefly discussing the basic concepts underlying the various multiple resonance experiments, a comparison is given of the hyperfine structure of in vitro prepared radical cations and anions of bacteriochlorophyll and bacteriopheophytin and of in vivo generated radicals of intact reaction centers. Finally, strategy and first results of CIDEP-enhanced-ENDOR on transient p-benzosemiquinone radicals will be presented.

105 A TIME-RESOLVED EPR STUDY ON THE NON PHOSPHORESCENT TRIPLET STATES: ORTHO DIAZAAROMATICS.

S. Yamauchi, M. Terazima and N. Hirota, Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan

Ortho diazaaromatics such as phthalazine (PH) and 9,10-diazaphenanthrene (DAP) do not phosphoresce in non polar media and their lowest triplet(T_1) states are supposed to have very short lifetimes. We have studied their T_1 states in the biphenyl host by means of time-resolved EPR with excimer laser excitation.



The zero field splittings (ZFS) determined from the angular dependence of the EPR signals are: D = 0.002 cm^{-1} and E = 0.024 cm^{-1} for PH and D = -0.129 cm^{-1} and E = 0.087 cm^{-1} for DAP, respectively. These ZFS are very different from those of the ordinary $\pi\pi^*$ aromatics. Large hyperfine splittings (HFS) due to two nitrogen nuclei are observed with the applied magnetic field (H) in the molecular planes. They are 13 G for PH (H//Y) and 24 G for DAP (H//Z), respectively. These results indicate that the T_1 state of DAP has a dominant $n\pi^*$ character and that of phthalazine a large $n\pi^*$ character. The lifetimes of these triplet states are estimated to be in the order of microsecond. Because of very efficient $T_1 \rightarrow S_0$ radiationless transition these triplet states are non phosphorescent in spite of their large $n\pi^*$ characters.

106 THE INTERPRETATION OF CIDEP SPECTRA

K.A. McLauchlan, Physical Chemistry Laboratory, South Parks Rd., Oxford OX1 3QZ

A novel flash-photolysis experiment will be described in which the high-resolution spectra of transient free radicals are obtained by time-integration of decay signals following laser pulses as the magnetic field is advanced digitally in a modified Bruker spectrometer. The method has unique sensitivity and resolution on the microsecond timescale.

All transient radicals exhibit spin-polarization (CIDEP) effects on their intensities immediately after the flash and the basic concepts of its origins will be discussed with brief summaries of the Triplet Mechanism and of the geminate and F-pair Radical Pair Mechanism. Their predictions will be compared with experiment for a number of situations including radicals observed in the photolysis of diazabenzenes and diazanaphthalenes where the theory is wholly consistent with some spectra of remarkable appearance. Participation of both excited singlet and triplet states of theparent molecules are revealed.

When aliphatic ketones are irradiated complex and changing CIDEP behaviour is observed at times up to 200 μs after the flash. The observations are unexpected and cannot be rationalised completely using accepted theory; their implications will be discussed.

Un-predicted experimental results will be presented from other experimental systems, as time allows.

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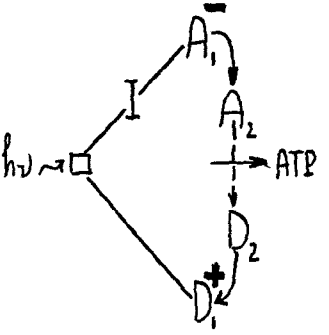
107 ELECTRON SPIN-ECHO CHARACTERIZATION OF COLLISIONS BETWEEN REACTIVE RADICALS IN SOLUTION.* David M. Bartels and Alexander D. Trifunac, Chemistry Division, Argonne National Laboratory, Argonne, IL 60439; Ronald G. Lawler, Chemistry Department, Brown University, Providence, RI 02912

Radical-radical encounters in solutions may be reactive or non-reactive, depending largely on the spin configuration of the radical pair. Non-reactive encounters both polarize the spin system by Chemically Induced Dynamic Electron Polarization (CIDEP) and cause spin dephasing by Heisenberg Exchange. Observation of these phenomena constitutes a probe of the diffusive nature of the radical encounters. We present time-resolved spin-echo measurements on some reactive free radical products of pulse radiolysis of aqueous solutions. The data allows us to assess directly, for the first time, the relative importance of reactive and non-reactive encounters between transient radicals in solution. The new information can be used to test various theoretical models of reactive diffusion.

*Work at ANL performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Science, US-DOE under Contract Number W-31-109-ENG-38.

108 IDENTIFICATION AND CHARACTERIZATION OF THE PRIMARY REACTANTS IN BACTERIAL PHOTOSYNTHESIS.* G. Feher, Dept. of Physics, U.C.S.D., La Jolla, CA 92093.

Bacterial photosynthesis can be schematically represented as shown in the Figure. A photon, $h\nu$, produces a charge separation by removing an electron from the donor, D_1. The electron cascades via the various acceptors, I, A_1, A_2, ..., etc. (and ultimately recombines with the hole on D_1^+) in what is known as the electron transfer chain. This process is coupled to the production of high energy compounds (ATP). During this cycle, each of the reactants (e.g., $D_1^+ A_1^-$, as indicated in the Figure) becomes paramagnetic and hence amenable to being investigated by EPR techniques. Examples of the identification and characterization of some of the reactants by EPR and ENDOR will be presented. Special emphasis will be given to D_1, which is a bacteriochlorophyll dimer, and to A_1 and A_2, which are quinones antiferromagnetically coupled to a high spin Fe^{2+}.



*Work supported by grants from the NSF and the NIH.

109 EPR AND ENDOR CHARACTERISTICS OF SIGNALS I AND II IN SPINACH CHLOROPLASTS. P. J. O'Malley and G. T. Babcock, Department of Chemistry, Michigan State University, East Lansing, MI 48824-1322.

Proton ENDOR spectra of Signal I ($P700^+$) in spinach chloroplasts and in Photosystem I particles have been obtained and compared with the corresponding ENDOR spectrum of monomeric chlorophyll a^+ cation radical. The hyperfine couplings for $P700^+$ can be interpreted in terms of those expected for a monomer Chl a^+ radical. The reduction in α carbon spin densities observed for the *in vivo* species when compared to the *in vitro* radical is attributed to differences in the composition of the ground state orbital for the two systems. For $P700^+$, a mixture of 75% D_0 and 25% D_1, where D_0 and D_1 represent the ground and first excited state orbitals calculated by Petke et al for Chl a^+ (Photochem. Photobiol. 31, 243-257 (1980)), gives good agreement between calculated and experimental spin density reduction factors. By an analogous treatment the magnetic resonance properties of $P680^+$ in Photosystem II and $P870^+$ in bacterial reaction centers can be interpreted as arising from monomeric structures. EPR and ENDOR studies of Signal II and certain cationic quinone radicals indicate that the molecular species giving rise to Signal II is a plastoquinone cation radical. Treating the quinone radicals as perturbed benzene cation radicals we show that stabilization of the antisymmetric orbital results in band shape and microwave power saturation characteristics similar to that observed for Signal II.

110 MAGNETIC MEASUREMENTS ON THULIUM NICOTINATE DIHYDRATE

C.A. Hutchison, Jr., Department of Chemistry, Chicago University, Illinois 60637;
J.M. Baker, B. Bleaney, J.S. Brown, M.J.M. Leask, P.M. Martineau and M.R. Wells,
Clarendon Laboratory, Oxford University, OX1 3PU, U.K.

Magnetic susceptibility and optical absorption measurements, and EPR spectra at 20 MHz,8,17 and 35 GHz have been used to investigate thulium nicotinate dihydrate, $[Tm(C_5H_4NCO_2)_3(H_2O)_2]_2$. Excited states ($^1G_4$) of each Tm^{3+} ion are all non-degenerate, but in spite of the low site symmetry, the lowest level of the ground manifold $^7F_6$ is found to be a non-Kramers doublet. X-ray measurements (Hutchison, Marin and Prout, in publication) show that the Tm ions occur in relatively isolated dimeric pairs, with ionic separation 0.4346 nm. The interaction between the two members of each dimer is mainly dipolar, the level with antiparallel spins lying 0.86(2) cm^{-1} above that with parallel spins. Along the dimer axis, g has its maximum value of 13.1(4). The resonance line at 20 MHz, like those at GHz frequencies, is an ESR transition from parallel to anti-parallel spin states. No long-range magnetic order is observed down to 0.55 K.

111 EPR STUDIES ON PAIRS OF JAHN-TELLER DISTORTED HEXAKIS PYRIDINE-N-OXIDE COPPER(II), $Cu(C_5H_5NO)_6^{2+}$ IONS. E. de Boer, C.P. Keijzers, G. van Kalkeren and J.S. Wood,
Department of Molecular Spectroscopy, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Semi-dilute 10 per cent $^{63}Cu:Zn(pyO)_6X_2$ (pyO=C_5H_5NO, pyridine-N-oxide), with X^-=ClO_4^- or BF_4^-, has been studied by X- and Q-band EPR. Below the transition from dynamic to static Jahn-Teller distortion (at ~ 60 K), pairs of $Cu(pyO)_6^{2+}$ ions are observed in both systems. In the ClO_4^- salt which is antiferrodistortively ordered in the pure copper crystal, antiferrodistortive pairs and a small amount of ferrodistortive pairs are detected. For both types of pairs all types of configurations are found to exist except the ones with the largest possible exchange interaction. However, in the BF_4^- salt all configurations do appear with similar intensities, whereas the pure copper system is ferrodistortive. From the AB type of spectra which are observed at Q-band, for both the ClO_4^- and BF_4^- complexes the weak exchange interaction in antiferrodistortive pairs could be determined: $|J'|k$= 0.041 K and 0.032 K, respectively. For the ClO_4^- salt this exchange coupling constant corresponds to the *inter*chain constant existing in the pure copper system which is known to be a pseudo-one-dimensional antiferromagnet at low temperatures. The above conclustions are drawn from a comparison between experimental and calculated spectra.

112 TIME-RESOLVED ESR ON LOW-DIMENSIONAL SOLIDS.
M. MEHRING, Physikal.Institut 2, Univ. Stuttgart,
7000 Stuttgart 80, Fed.Rep.Germany.

Time resolved ESR experiments (spin-echo, saturation recovery, spin echo modulation etc.) have been performed on several low-dimensional solids. Among these are cis- and trans-polyacetylene from which spin-echo spectra were obtained, which allowed to separate three distinct paramagnetic species, i.e. chain defects, trapped soliton or polaron, mobile soliton. The temperature dependence of the spin lattice relaxation of these species was determined. Some preliminary results on one-dimensional radical cation salts will also be reported.

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113 SPIN DYNAMICS IN CONDUCTING POLYMER COMPOSITES: ELECTRON SPIN ECHO STUDIES OF POLYACETYLENE IN POLYETHYLENE. H. Thomann, H. I. Kim, A. Morrobel-Sosa, C. Chiu, L. R. Dalton, M. E. Calvin, and G. E. Wnek, University of Southern California, Los Angeles, CA.

The spin dynamics for the paramagnetic defect in composites of low density polyethylene, LDPE, and trans-polyacetylene, t-$(CH)_x$, prepared by polymerization of acetylene in LDPE films impregnated with a Ziegler-Natta catalyst, have been studied as a function of t-$(CH)_x$ concentration over the temperature range of 300°K to 4°K. Although samples were prepared at high temperature where only the thermodynamically stable trans-$(CH)_x$ isomer is normally formed, the spin dynamics are not identical to the dynamics measured in pure t-$(CH)_x$. ESE phase memory (T_m) and ESE spin-lattice (T_{1e}) relaxation times are observed to be a function of t-$(CH)_x$ concentration in the host polymer matrix, however, a smooth transition towards the behaviour observed for pure t-$(CH)_x$ is apparent. The implications of the present results for soliton diffusion are explored. We also consider the importance of other dynamic processes such as electron Heisenberg spin exchange, electron dipolar interactions, and nuclear spin diffusion in determining the observed experimental results.

114 SPIN LATTICE RELAXATION IN QUASI-ONE-DIMENSIONAL π-ELECTRON ORGANIC SEMICONDUCTORS. B. H. Robinson, Department of Chemistry, University of Washington, Seattle, WA and H. Thomann, Department of Chemistry, University of Southern California, Los Angeles, CA.

We have recently investigated the dependence of the spin-spin and spin-lattice relaxaction rates in polyacetylenes (CHx) by the Electron Spin Echo (ESE) technique on temperature, microwave frequency, ratio of cis to trans forms and fraction of co-polymer (polyethylene). The spin-spin relaxation times will be compared to the jumping times predicted by a simple two-site jump model. The motional energy barrier is estimated by both an Arrhenius and an Eyring type model. Results suggest that spin-spin relaxation times are dominated by electron diffusion. We consider that the regions of conductivity may be highly interrupted by the presence of a co-polymer or the cis (non-conductive) form. Other lattice impurities may also be responsible for disruption of the conducting properties of pure trans-polyacetylene. We therefore consider an interrupted strand model. Within the context of the interrupted strand model, spin-lattice relaxation is analyzed in terms of spin-diffusion, lattice diffusion, and a spin-spin interaction which is dominated by the dipolar interaction. Scalar coupled interactions will be discussed, but they are probably not significant. The comparison of spin-spin and spin-lattice relaxation time scales suggests the possibility of two modes of relaxation. One mode is due to spin-diffusion where the electron moves on a static lattice, the second is due to the lattice which can relax either a stationary or a moving electron. These two processes have independent time scales and are compared in terms of the possibility of different relaxation mechanisms for spin-spin and spin-lattice relaxation times. Finally, a comparison is made with ENDOR data on these systems and the possibility of the electron behaving as a neutral soliton is considered.

115 DIPOLAR CORRELATION FUNCTIONS AND SPIN RELAXATION RATES FOR FINITE TWO-DIMENSIONAL SYSTEMS.

J.-P. KORB[+] AND H.M. McCONNELL[++]
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++ Stauffer Laboratory for Physical Chemistry, Stanford University, Stanford, California 94305, U.S.A.

A statistical treatment (1) is used to describe the intermolecular dipole-dipole relaxation process of spins diffusing laterally on the surface of a sphere. Convergent expressions of the spin-spin T_2^{-1} and spin-lattice T_1^{-1} relaxation rates are found , even at frequencies close to zero, in opposition to the logarithmic divergence of these rates for infinite surfaces. We present theoretical variations of these rates with the Larmor frequency and the lateral diffusion coefficient. These variations compared with those of tri-dimensional systems shows a diminution of T_1 and an important shortening of T_2 which stays always shorter than T_1 even in the extreme narrowing case. Our theoretical results can be very useful for those who are interested in how magnetic resonance might be employed to study restricted motion of molecules physisorbed on quasi-spherical homogeneous surfaces or for spin labels embedded in biological vesicular membranes.

(1) J.-P. KORB, D.C. TORNEY and H.M. McCONNELL, J. Chem. Phys. (in press).

116 "MAGNETIC EXCHANGE ANISOTROPIES AS DETERMINED BY EPR", John E. Drumheller, Dept. of Physics, Montana State U., Bozeman, MT 59717.

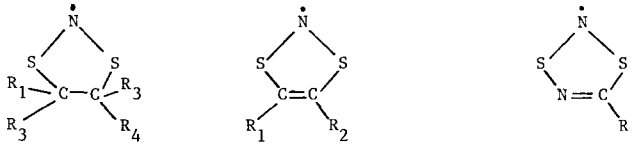
The epr linewidth versus angle in certain non-diffusive exchange narrowed magnetic systems yields information about the magnetic anisotropies that is not extractable from other magnetic measurements. Within the approximation of static spin correlation, inclusion of axial and orthorhombic anisotropic exchange as well as antisymmetric exchange terms in the Hamiltonian yield contribution to the second moment and therefore the linewidths that are rich in angle dependence and from which the magnitude and direction of the anisotropies can be found. Recent data will be presented on several weakly exchanged one-dimensional spin 1/2, Heisenberg ferromagnets such as TMACuC and CHAC as well as a review and the results on the two-dimensional layered eclipsed compounds of nDACuC.

117 EPR INVESTIGATION OF THE CESIUM-AMMONIA SYSTEM. P. Hsu, W. Glaunsinger, Dept. of Chem., ASU, Tempe, AZ 85287, K. Burton, R. Catterall, Dept. of Chem., U. of S. Salford, U.K. M 54 WT.

EPR spectroscopy has been used to investigate cesium-ammonia solutions over a wide range of compositions [≥0-10 mole percent metal] (MPM) . In very dilute solutions ($\leq 10^{-4}$MPM) EPR spectra characteristic of isolated solvated electrons have been observed. As the metallic concentration is increased the EPR signal broadens dramatically, which results from interactions of the solvated electrons with the cesium ions in these solutions. In the concentration range 2 - 6 MPM there is a continuous nonmetal-to-metal transition. Above 6 MPM conduction electron spin resonance signals have been observed in these solutions. The EPR spectra in these solutions can be interpreted in terms of the spin-orbit coupling between the electrons and the cesium ions.

118 ESR AND ENDOR INVESTIGATIONS OF STABLE FREE RADICALS FORMED FROM SULPHUR-NITROGEN HETEROCYCLES, L. H. Sutcliffe, Donnan Chemistry Laboratories, The University, Liverpool L69 3BX, England.

Three main classes of novel long-lived free radicals have been discovered, namely:



The radicals have simple ESR spectra and are potentially useful spin probes or labels: they are also useful model compounds for detailed studies of rotational correlation times and they give well-resolved powder spectra. We have developed means of isotopic labelling the radicals with nitrogen-15, sulphur-33, deuterium and carbon-13. ENDOR spectroscopy has been used to obtain precise hyperfine coupling constants and to determine their relative signs. Temperature coefficients of the coupling constants have been measured and INDO calculations have shown that nitrogen out-of-plane wagging is responsible.

119 NUCLEAR QUADRUPOLE INTERACTIONS IN ELECTRON SPIN ECHO SPECTRA OF SOLIDS*. M.K. Bowman, Chemistry Division, Argonne National Laboratory, Argonne, IL 60439

Nuclear quadrupole interactions have two effects on electron spin echo envelope modulation spectra in solids. (1) The nuclear eigenfrequencies present in the modulation are altered or split by the nuclear quadrupole interaction. (2) The intensities of those eigenfrequencies are changed, even to the extent that modulation is possible in the absence of an electron nuclear dipolar interaction. A very fast, general method of calculating modulation spectra for I=1 nuclei is presented and is used to interpret modulation from ^{14}N and ^{2}H nuclei. The angle between the non-coaxial quadrupole and hyperfine tensors can provide a great deal of insight into free radical solvation in solids.

*Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy under contract W-31-109-ENG-38.

120 ESR SPECTRA, CHEMICAL PROPERTIES AND SPIN PROBE POTENTIAL OF A SERIES OF DISULPHENIMIDYL FREE RADICALS. S. R. Harrison, R. S. Pilkington and L. H. Sutcliffe, Donnan Chemistry Laboratories, The University, Liverpool, L69 3BX, England.

We have shown that the non-polar nature, the sharp spectral lines, the ease of nitrogen-15 substitution and the large A and g tensor anisotropies of a series of 4,5-disubstituted-1,3,2-dithiazolyl radicals (A) makes them potential spin probes (S. A. Fairhurst, R. S. Pilkington, L. H. Sutcliffe, J. Chem. Soc. Faraday I, 79, 439 (1983)). The contribution compares the ESR spectra, effective radii (calculated from motionally broadened spectra) and chemical properties of the above dithiazolyl radicals (A) with three others containing the SNS fragment, namely dibenzene sulphenamidyl (B), our recently discovered 5-methyl-1,3,2-benzodithiazol-2-yl (C) and 4-methyl-1,3,2,5-dithiadiazol-2-yl (D) radicals. Room temperature spectra of all the radical solutions have the simple 3-line spectra required for spin probes but the lines of B, C, and D are broadened by unresolved coupling. Cooling to -60°C allows the fine structure to be resolved. All the radicals can be handled in air and persist for at least a week in solution under vacuum at room temperature. Only radicals of type C can tolerate water. All radicals are stable to ultraviolet radiation except radicals type B. Using tumbling theory, the asymmetric line broadened ESR spectra of the radicals give radii in reasonable agreement with the expected values.

121 AN ELECTRON SPIN RESONANCE STUDY OF ORGANO-SULFUR RADICALS PRODUCED IN ELECTRON-IRRADIATED AQUEOUS SOLUTIONS. SPIN TRAPPING WITH NITROMETHANE ACI-ANION AND 2-METHYL-2-NITROSOPROPANE.

Hitoshi Taniguchi, Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556

Free radicals produced by reaction of OH radical with 18 organo-sulfur compounds containing -CSSC-, -CSH, or -CSC- groups in N_2O-saturated aqueous solutions have been studied using in situ radiolysis-steady state ESR method. Although organo-sulfur radicals (RS•) are considered to be principally formed, they cannot be observed directly in aqueous solutions because of the line broadening caused by the g factor anisotropy. They can, however, be detected indirectly by spin trapping technique using nitromethane aci-anion [CH_2=NO_2^-] and 2-methyl-2-nitrosopropane [$(CH_3)_3$ CN=O] as spin trapping reagents. ESR parameters of spin adducts RS-$CH_2NO_2^-$ are as follows: a^N=23.98-24.29 G, $a^H(CH_2)$ = 5.70-7.10 G, a^H(-CHS-CH_2)= 0.65-0.83 G, and g=2.00557-2.00566. Inequivalent hyperfine coupling constants of methylene protons adjacent to nitrogen and selective line broadening in ESR spectra can be attributed to the chiral carbon atom across a sulfur atom from the methylene group or hindered internal rotation around the C-N bond. ESR parameters of spin adducts RS-N(O•)C$(CH_3)_3$ are a^N = 17.91-18.40 G, a^H(-CHS-N<) ≤ 1.36 G, and g = 2.00646-2.00656. The apparent differences in the trapping efficiency of RS• from disulfides, mercaptans, and sulfides by the above two spin traps are discussed.

122 SITE LOCATION OF THE TRAPPED ELECTRON IN X-RAY IRRADIATED SINGLE CRYSTALS OF RHAMNOSE AND TREHALOSE. L. D. Kispert and P.-O. Samskog, Chemistry Department, University of Alabama, Tuscaloosa, AL 35486 and A. Lund, Studsvik Science Research Laboratory, S-61182 Nykoping, Sweden.

It has been shown by EPR and ENDOR measurements that electrons can be stabilized in single crystals of polyhydroxy compounds at 4.2 K. The electron is trapped in an intermolecular site by polarization forces arising from nearby hydroxy groups. When the electron decays, the reaction product is a hydroxy alkyl radical. Until recently, it was not possible to identify the exact location of the trapped electron. However we have been able to identify a preferred trapping site in x-ray irradiated trehalose and rhamnose single crystals. In irradiated trehalose, the electron is trapped in an intermolecular site between an OH group (2') of trehalose and a water of crystallization. The electron trap in rhamnose is formed by three hydroxyl groups, two on the carbohydrate and one on a water molecule. In both cases, the trapped electron decays by reaction with one of the protons forming the trap. In trehalose this decay is via cleavage of an OH (2') bond attached to the carbohydrate and the liberated hydrogen atom abstracts an adjacent hydrogen atom on C_3'. In rhamnose a similar behavior occurs, however the liberated hydrogen atom abstracts a hydrogen from the same carbon to which the OH is attached. The important conclusion is that the electron trap is pre-existing in the crystal lattice of both crystals and no reorientation of OH dipoles is necessary to stabilize the electron.

123 EPR OF THERMAL DECOMPOSITION PRODUCTS FROM ENERGETIC MATERIALS, Part I. M.D. Pace, A. D. Britt, and W. B. Moniz. Naval Research Laboratory, 4555 Overlook Avenue, Washington, D. C. 20375.

EPR experiments have shown that free-radicals are produced during the thermal decomposition of energetic nitramines. Unfortunately the identification of the radicals is hindered by their rapid rate of decay (many with life-times less than 10^{-6} seconds). Basic time-resolved techniques such as scanning H_o rapidly or detecting the dc signal allow spectral information to be recorded with a fast time response. Results from studies on cyclotrimethylenetrinitramine ($C_3H_6N_6O_6$, RDX) and triaminotrinitrobenzene ($C_6H_6N_6O_6$, TATB) will be presented.

124 MAGNETIC RESONANCE STUDY OF NATIVE AND CARBONIZED ILLINOIS COALS.* R. B. Clarkson and Edward Duliba, Department of Chemistry, University of Illinois, Urbana, Illinois 61801

A technique for the removal of organic sulfur from Illinois bituminous coal by low-temperature carbonization has been proposed by Kruse and Shimp (Coal Processing Technology, Vol. VII, A Chemical Engineering Progress Technical Manual, AIChE, 1981, pg 124-134). As part of an on-going program aimed at developing techniques for the study of coal structure, we have followed this thermal desulfurization process using a variety of EPR and NMR techniques, as well as other spectroscopies.

The X and Q-band EPR spectra of coals have been studied as a function of carbonization temperature, and g-value changes have been compared to changes in the heteroatom concentration. In some cases, the carbonization process has been studied in situ by means of a high-temperature reactor placed within the EPR cavity. Electron Spin Echo (ESE) spectra of the processed coals also have been investigated at a variety of temperatures. GC/FTIR of condensed volatiles evolved in the process has been done, and Mössbauer spectra have been taken.

*This work was sponsored by a grant from the Center for Research on Sulfur in Coal, Illinois Coal Research Board.

125 Abstract not available.

126 TEMPERATURE DEPENDENT VIBRONIC EFFECTS IN THE EPR OF A SOLID MIXED VALENCE BENZOTRIAZOLATO COPPER COMPLEX. J. Baranowski, F. Padula, C. Goldstein and G. Kokoszka, Chemistry Dept., SUNY Plattsburgh, NY 12901 and A. Siedle, 3M Central Research Laboratory, St. Paul, MN 55101.

EPR linewidths have been used to characterize the motional dynamics of metal complexes in liquids and the general theory has been reasonably well understood for nearly twenty years (P. Atkins and D. Kivelson, J. Chem. Phys. 1966, 44, 169). In copper(II) complexes, the experimental feature which has been often used to monitor these dynamical effects is the linewidth variation of the four-line "isotropic" EPR spectrum associated with each of the four hyperfine (M_I) spectral components. Often the details of the molecular geometry are not known with great precision because the paramagnetic ions which serve as probes are in solution. The observation of an M_I dependent linewidth variation in the crystallographically well characterized $Cu_5(BTA)_6(t\text{-}C_4H_9NC)_4$ solid compound in the 128-300°K range (J. Am. Chem. Soc. 1983, in press) has prompted a detailed temperature dependent study of the changes in the epr spectra and the development of a computer program incorporating linewidth and lineshape changes as a function of temperature as well as M_I. The results of this study will be seen to be generally consistent with the earlier theoretical models but vibronic rather than rotational modes provide the basis for the dynamical molecular effects observed.

127 JAHN-TELLER EFFECT IN $Cu(N_6C_{12}H_{30})(ClO_4)_2 \cdot C_6H_6$. G. Kokoszka, C. Goldstein, and F. Padula, Chemistry Dept., SUNY Plattsburgh, NY 12901 and J. Bulkowski, A. Rheingold, and L. Burmeister, Chemistry Dept., Univ. of Delaware, Newark, DE 19711.

An x-ray study of the title complex indicates that the Cu(II) ion is coordinated to a hexadentate ligand and that the Cu(II) ion occupies a special position in the unit cell. The latter belongs to a hexagonal space group R3 with a = 9.799 and c = 22.208. The three-fold symmetry and the large Cu(II)-Cu(II) distance (over 9Å) provide a unique opportunity to investigate the dynamical Jahn-Teller effect with minimum interference from low symmetry intermolecular effects or complications due to electronic exchange effects. The epr studies were carried out in the 4-300°K temperature range at 9 GHz and at higher microwave frequencies in the 77-300°K range. At low temperatures, the tetragonal spectrum was observed but had already been partially averaged by the vibronic activity at 77°K. In the upper third of the temperature range the spectrum was a structureless Lorentzian line with a linewidth that had a peak to peak value of over 600 gauss at 300°K and displayed a temperature dependence of the form exp(-E/kt) where E is about 250 cm^{-1}. This suggests an Orbach relaxation mechanism but the value of E is over 4 times smaller than had been previously reported for a molecular Cu(II) complex. This is presumed to be a direct result of the greatly constrained intramolecular vibrations available to the hexadentate Cu(II) complex.

128 THE NATURE OF THE JAHN-TELLER EFFECT IN THE COPPER DOPED HEXAIMIDAZOLE ZINC DICHLORIDE TETRAHYDRATE COMPLEX. E. de Boer, C.P. Keijzers, T. Jansen, G. van Kalkeren and J.S. Wood, *Department of Molecular Spectroscopy, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands*

The $Cu(Im)_6^{2+}$ (Im=Imidazole) ion doped into the triclinic zinc host crystal $Zn(Im)_6Cl_2 \cdot 4H_2O$ has been reexamined with X- and Q-band single crystal EPR spectroscopy over the temperature range 4-300 K. Contrary to the earlier study, which characterized this system as an example of Jahn-Teller tunnelling between three tetragonally elongated configurations, it has been found from our more extensive measurements, that the $Cu(Im)_6^{2+}$ ion represents *an example of strong Jahn-Teller coupling. Below the transition temperature from dynamic* to static behaviour, two wells in the 'Mexican hat' potential energy surface are preferentially and almost equally occupied. The g and hyperfine tensors for these two sites are consistent with the tetragonally elongated geometry typically found for the static Jahn-Teller effect in CuL_6^{2+} systems. At higher temperatures the third site becomes populated leading to a near isotropic spectrum at room temperature. Measurement of the variation of g and hyperfine coupling with temperature leads to an approximate value of 100-150 cm^{-1} for the height of the barrier separating this third site from the two lower energy sites. *Examination of the structure of the host crystal allows an understanding of the observed* ESR behaviour.

129 SINGLE CRYSTAL EPR SPECTRA OF SPIN-LABELED METALLOPORPHYRINS. R. Damoder, K. M. More, G. R. Eaton, Department of Chemistry, University of Denver, Denver, CO 80208 and S. S. Eaton, Department of Chemistry, University of Colorado at Denver, Denver, CO 80202.

Vanadyl, copper, and silver complexes of two spin-labeled porphyrins were doped into ZnTPP. The orientation dependence of the electron-electron spin-spin interaction was analyzed to obtain the isotropic exchange and anisotropic dipolar contributions to the interaction. The interspin distances were 9.2 to 15.5 Å. The values of the exchange coupling constant J ranged from $+12 \times 10^{-4}$ cm^{-1} (ferromagnetic) to -35×10^{-4} cm^{-1} (antiferromagnetic).

130 SPIN-LABELED COMPLEXES OF IRON(III) AND NICKEL(II), L. Fielding, K. M. More, P. Smith, G. R. Eaton, Department of Chemistry, University of Denver, Denver, CO 80208 and S. S. Eaton, Department of Chemistry, University of Colorado at Denver, Denver, CO 80202.

In fluid solution strong spin-spin interaction between a nitroxyl radical and a rapidly relaxing metal such as iron(III) or nickel(II) causes severe broadening of the nitroxyl EPR signal. A series of complexes has been prepared to examine the dependence of the broadening on a) the distance between the transition metal and the radical and b) the bonding pathway between the two centers. Solution equilibria involving these complexes have also been examined.

DRUG MEDIATED SUPEROXIDE PRODUCTION. G.M. Rosen and E.J. Rauckman, Duke University, Durham, N.C. et al.: 25th RMC Abstracts and Meeting Program

131 The production of superoxide appears to be a ubiquitous event during intracellular one-electron redox reactions. In the presence of drugs that are capable of undergoing one-electron redox reactions, the intracellular generation of superoxide may be significantly increased. Three such drugs are cocaine, acetaminophen and nitrazepam, which when biotransformed to reactive intermediates enhance the production of superoxide by either indirect or direct reductive pathways. The ability to detect superoxide in biological milieu is filled with a number of difficult problems. For example, the ferricytochrome c assay method cannot be used in the presence of NADPH-cytochrome P-450 reductase since cytochrome c is preferentially reduced by this enzyme. We have found that the superoxide-dependent oxidation of one particular hydroxylamine, 2-ethyl-2,5,5-trimethyl-3-oxazolidine, to its corresponding nitroxide, 2-ethyl-2,5,5-trimethyl-3-oxazolidinoxyl, can be used to quantitate superoxide production by hepatic microsomes and purified enzymes. We determined that this assay method is free from most of the problems inherent in other methods for the identification of superoxide. Finally, spin trapping methods will be examined as an additional technique to monitor superoxide production in biological milieu catalyzed by cocaine, acetaminophen and nitrazepam metabolites. Difficulties using spin trapping methods will be explored.

CHARACTERIZATION OF MOTION OF ^{15}N-SUBSTITUTED STEARIC ACID SPIN LABELS BOUND TO PROTEINS AND MEMBRANE BILAYERS. J.H. Park, S.D. Venkataramu, C.R.Park, N. Abumrad, and A.H. Beth, Vanderbilt University, Nashville, TN 37232

132 In order to improve the motional characterization of biological membranes, model lipid bilayers, and protein-lipid interactions, we synthesized four ^{15}N-nitroxyl spin labels: 5-nitroxyl stearate (^{15}N-5-NS), 12-nitroxyl stearate (^{15}N-12-NS), 16-nitroxyl stearate (^{15}N-16-NS) and ^{15}N-cholestane. In all cases, the signal height of the ^{15}N-spin label was approximately 1.7 fold greater than that of the commerically available ^{14}N counterpart. With ^{15}N-stearic acid probes bound to bovine serum albumin the spectral intensity was increased 1.4 fold over the τ_c range of 8×10^{-8} to 1×5^{-5} sec. The resolution was sufficiently enhanced to permit direct measurement of A and g tensors which greatly facilitated computer simulations of EPR and ST-EPR spectra. With the insertion of ^{15}N-5-NS into erythrocyte membranes, the spectral simplification from a three line to a two line response practially eliminated overlap of the two nuclear manifolds and permitted determination of both $A_{||}$ and $A_{\perp}$ by direct inspection. With ^{14}N-5-NS measurements of $A_{\perp}$ are complicated by overlaps of the three manifolds in the central region of the spectrum. Moveover, the ST-EPR spectrum of ^{15}N-5-NS showed enhanced resolution and 3 to 4 fold sensitivity increases in the L, L', L" regions compared to the ^{14}N-probe. In collaboration with J. Feix, C. Popp and J.S. Hyde, lateral diffusion and vertical fluctuations of stearic acid spin labels in the model DMPC membranes have been studied using ELDOR spectroscopy and various combinations of ^{14}N and ^{15}N spin probes (Fed. Proc., ASBC, 1983). Collisions between ^{14}N and ^{15}N spin labels were observable as reductions in signal intensities and could be analyzed quantitatively. Thus, ^{15}N spin labels, either singly or in combination with ^{14}N probes, afford considerable advantages in detailed spectral analyses.

133 THE EFFECTS OF INTERNAL MOTION... REGIMES. P. H. Robinson, Department of ... WA 98195 and A. H. Beth, Department of Physiology, Vanderbilt ... 37232.

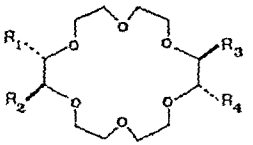
Motional Processes of vibrations about bonds with limited amplitudes appear in many spin label studies. We consider the cases where a spin-label is attached to a large rigid object. The attachment is flexible due to a set of bonds, each of which has a limited amplitude of motion. We present a theoretical formalism which incorporates limited amplitude vibrations around a series of bonds. The simplest example is the accumulative effect of librations about a common axis for many rotating bonds. Spectra are simulated based on this model and compared with anisotropic rigid-body spectra. For large numbers of bonds this model is equivalent to the continuously twistable cable model. It is valid in the limit of a small number of flexible bonds. We compare these results with pre-averaging models and indicate problems with such models. In general, internal motion creates a locally non-Markoffian operator. Such models are treated by using auto- and cross-correlation functions. One needs a very large number of these functions (which for complicated motion are developed numerically). To simplify the treatment of these processes we have developed an infinite summed expression for the higher order terms. This summed form of the higher order correlation functions has been tested directly on the Brownian and Strong Jump models. These two models reduce to analytic expressions which may then be compared with full matrix numerical calculations which demonstrates the validity of the summation technique. This results in a considerable reduction in computer run time and correlation functions.

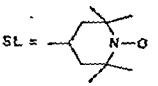
134 SPIN TRAPPING AND DIRECT ELECTRON SPIN RESONANCE INVESTIGATIONS OF THE PHOTOREDUCTION OF GENTIAN (CRYSTAL) VIOLET. Volker Fischer, Willard G. Harrelson, Jr., Colin F. Chignell, and Ronald P. Mason. Laboratory of Environmental Biophysics, NIEHS, P.O. Box 12233, Research Triangle Park, N.C. 27709

The photolysis of gentian violet (crystal violet) has been studied in aqueous solution by ESR spectroscopy. The photoreduction of gentian violet to the semireduced carbon-centered radical was detected with ESR under anaerobic conditions. The quantum yield of radical formation could be greatly increased by physiological reducing agents, such as NADH and cysteine. The radical is insoluble in buffer, and the effects of detergents and liposomes on its solubility were studied. Although no gentian violet radical could be detected under aerobic conditions, the superoxide dismutase-sensitive DMPO-superoxide spin adduct was found. Apparently the gentian violet radical is formed under aerobic conditions, but it is oxidized by oxygen, which would regenerate the dye and form superoxide.

135 SYNTHESIS AND EPR STUDIES OF CHIRAL DINITROXIDE CROWN ETHER. H. Dugas, M. Ptak*, and P. Keroack, Department of Chemistry, Université de Montréal, Montreal, Canada and Centre de Biophysique Moleculaire*, CNRS, Orleans, France.

The synthesis of syn and anti chiral dinitroxide [18]-crown-6 ethers and of a tetranitroxide crown ether is described. The presence of a spin-spin interaction for the syn-isomer makes this new paramagnetic probe particularly useful to follow by epr the effects of K^+ ion binding, pH, solvent, and temperature. These observations are discussed in terms of a global dynamical fluctuation of the crown ether ring.





1 : $R_1=R_2=R_3=R_4=COOH$

2 : $R_1=R_4=COOH$, $R_2=R_3=CONH\text{-}SL$; DI-SL-SYN

3 : $R_1=R_3=COOH$, $R_2=R_4=CONH\text{-}SL$; DI-SL-ANTI

4 : $R_1=R_2=R_3=R_4=CONH\text{-}SL$; TETRA-SL

136 RECENT ADVANCES IN SOLID STATE ENDOR METHODOLOGY
A. Schweiger, ETH-Zürich, Universitätsstr. 22, CH-8092 Zürich, Switzerland

Conventional ENDOR has proved to be a very powerful tool to evaluate hyperfine and quadrupole coupling constants of paramagnetic species in single crystals and polycrystalline or frozen solution samples. In complex spin systems, however, the utility of this method is often limited due to the high density of resonance lines which complicates or even prevents the interpretation of the spectra.
Several novel ENDOR techniques have recently been developed in our laboratory which may either considerably simplify complicated ENDOR spectra by suppression of specific transitions or which may essentially improve the information contents of the spectra by additional labellings of the resonance lines.
The principles of the methods

- ENDOR with circularly polarized radio frequency fields (CP-ENDOR)
- Orientation modulated ENDOR (OM-ENDOR)
- Polarization modulated ENDOR (PM-ENDOR)
- Nuclear spin decoupling in ENDOR
- Nuclear Zeeman correlated ENDOR

will be presented and illustrated by several examples.

137 RECENT PROGRESS IN SOLUTION-ENDOR SPECTROSCOPY OF NON-PROTON NUCLEI. W. Lubitz, Institut für Organische Chemie, Freie Universität Berlin, West Germany

During the last decade ENDOR spectroscopy has become an important tool for the elucidation of the electronic structure of complex radicals in solution (K. Möbius, M. Plato, W. Lubitz, Phys. Rep. 87, 171 (1982)). In order to get a detailed spin density map it is necessary to detect not only the protons but also the other magnetic nuclei which are present in the radical under study. With this in mind a systematic experimental and theoretical investigation of the ENDOR sensitivity of various nuclei, namely, D, ^{13}C, ^{14}N, ^{19}F, ^{31}P and all alkali nuclei was presented in 1981 (M. Plato, W. Lubitz, K. Möbius, J. Phys. Chem. 85, 1202 (1981)). In this paper it is intended to give an overview of more recent developments in the field of solution-ENDOR of non-proton nuclei.
The first detection of ^{205}Tl (I=1/2, 70.5%) and ^{203}Tl (I=1/2, 29.5%) in tight ion pairs with o-semiquinones (K. B. Ulmschneider, H. B. Stegmann, K. Scheffler, G. Viertel, Z. Naturforsch. 33b, 237 (1978)) will be reported. Also ^{29}Si (I=1/2, 4.7%) could be detected in radical cations and anions of some trialkyl-silyl substituted olefins (H. Bock, W. Kaim, Acc. Chem. Res. 15, 9 (1982)) in natural abundance. Furthermore an ^{15}N (I=1/2, 0.37%) ENDOR study on ^{15}N labelled dithiazolidinyl radicals (R. S. Pilkington, L. H. Sutcliffe, Chem. Comm., in press) will be presented, and the possibility to detect other nuclei - like ^{33}S - in these systems discussed. Nuclei with large quadrupole moments are usually more difficult to observe. Here the first detection of ^{11}B (I=3/2, 80.42%) and ^{10}B (I=3, 19.58%) in the radical anion of pyrazine complexed with triethylboron (W. Kaim, Angew. Chem. 95, 201 (1983)) in solution will be described. Similar complexes with $M(CO)_5$ ligands (M=W, Mo) were investigated and the detectability of the metal nuclei will be discussed. The projects described were performed in cooperation with H. Stegmann (Tübingen, FRG), H. Bock, B. Hierholzer and W. Kaim (Frankfurt, FRG) and L. Sutcliffe (Liverpool, GB).

138 ENDOR STUDY OF PHOTO-EXCITED TRIPLETS RANDOMLY ORIENTED IN SOLID SOLUTION. T. K. Chandrashekar, B. Kirste, and H. van Willigen, Department of Chemistry, University of Massachusetts at Boston, Boston, MA 02125

With the aid of magneto-selection of orientation, high-resolution ENDOR spectra can be obtained of photo-excited triplet state molecules randomly oriented in solid solution. The spectra give information on hyperfine interactions providing an insight into the electronic structure of the triplets. Applications on systems with triplet-state lifetimes (τ_T) ranging from seconds (naphthalene) to less than one millisecond (cyano-substituted tetraphenylporphyrins) will be presented. It will be shown that in cases where τ_T is short (of the order of the electron-spin relaxation time), "spin-polarization" effects can cause a strong signal enhancement facilitating the measurements.

139 A REINVESTIGATION OF THE CONFORMATIONAL INTERCONVERSION IN 1,2,3,6,7,8-HEXAHYDRO-PYRENE CATION RADICAL BY CIDEP, ENDOR AND Magnetic Resonance and Vol. Mäkelä, Department of Chemistry, University of Jyväskylä, SF-40100 Jyväskylä 10, Finland

Rocky Mountain Conference on Magnetic Resonance

The conformational interconversion of hexahydropyrene cation radical has been reexamined by EPR and ENDOR spectroscopy and the Arrhenius plot is presented for a wider temperature range than earlier. The EPR spectra of cation radical were measured from -130 to +90 °C and ENDOR spectra from -130 to -10°C. The thermodynamic constants of the conformational interconversion of the cation radical were determined on the basis of the temperature dependent spectra and compared with those previously obtained by EPR spectroscopy (-89 to +25°C). The high resolution spectra clearly show that there are two overlapping spectra at low temperature, and this is confirmed by computer simulation.

140 TIME RESOLVED FLUORESCENCE DETECTED MAGNETIC RESONANCE (FDMR) OF TRANSIENT RADICAL IONS

Steven M. Lefkowitz and Alexander D. Trifunac
Chemistry Division, Argonne National Laboratory, Argonne, IL 60439

FDMR measures the fluorescence response of a scintillator system undergoing pulse radiolysis in nonpolar solvents to pulsed microwaves at a resonant magnetic field, to yield a superposition of the EPR spectra of a radical ion pair geminately recombining to give fluorescence. We have measured the EPR spectrum of the radical cation of cyclohexane, and by using trialkylamines as cation scavengers, have derived the EPR spectra of the trialkylaminium radicals. These results indicate the presence of a low mobility "trapped" cyclohexane radical cation, existing along with the higher mobility "delocalized" species, and suggest that triethylamine reacts only with the "trapped" species to give the triethylaminium radical.

141 BIOINORGANIC MODEL SYSTEMS: EPR OF 5 COORDINATE Cu(II) COMPLEXES WITH TRIPOD LIGANDS.

F. Padula, C. Goldstein and G. Kokoszka, Chemistry Dept. SUNY Plattsburgh, NY 12901 and K. Karlin, J. Hayes and J. Zubieta, Chemistry Dept., SUNY Albany, NY 12222.

Recent studies have emphasized the usefulness of tripod ligands in studying and modeling various aspects of Cu(I) and Cu(II) coordination chemistry (Inorg. Chem. 1983, 2, 4106). In this paper we report the results of an epr study and coordinate these results with x-ray crystallographic data on the sample $[Cu(tmpa)x]PF_6$ with tmpa = tris (2-pyridyl)-methylamine and x = Cl^-. The epr results on related tmpa complexes will also be presented. The studies on the Cl^- complex were carried out from 77 to 300°K in the 9-60 GHz range and over a 4 to 300°K temperature range at 9 GHz. Both frequency and temperature dependent effects were found in the non-diluted material and were associated with a 10/3 effect (J. Inorg. Nucl. Chem. 1974, 36, 1565). However, it is possible to extract the appropriate molecular magnetic parameters from such studies and to compare them with results obtained from the complex isolated in frozen glasses. The effect of intermolecular exchange effects on the g values will be described.

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142 LOW SPIN FERRIC PORPHYRIN COMPLEXES. ANALYSIS OF THE ELECTRONIC STRUCTURE BASED ON SINGLE-CRYSTAL EPR MEASUREMENTS. Marianne P. Byrn, Bradley A. Katz, Nancy L. Keder, Keith R. Levan, Charles J. Magurany, Kathleen M. Miller, Jeffrey W. Pritt, and Charles E. Strouse, Department of Chemistry and Biochemistry, UCLA, Los Angeles, California 90024.

Single-crystal EPR g-tensor determination for a low-spin ferric porphyrin complex can provide both an accurate description of spin distribution and a quantitative characterization of the axial ligand binding. Experimental g-tensor determinations for a series of six low-spin tetraphenylporphinatoiron(III) thiolate complexes illustrate the simple, but unintuitive, relationship between the orientation of the principal axes of the g-tensor and the spin distribution. The axial thiolate ligands in this series of complexes cover a relatively wide range of sigma donor strength. Analysis of the crystal field parameters obtained from the principal g-values reveals an excellent correlation between the tetragonality and the pK_a of the corresponding thiol. On the other hand, the rhombicity for this series of complexes is virtually independent of sigma donor strength of the axial ligand. This observation provides a basis for the prediction of spin density distribution in unsymmetrically ligated porphyrin complexes. Published single-crystal ESR data for several heme proteins are reevaluated in light of these results.

143 AN EPR INVESTIGATION OF $[Co^{III}(tpp)]^{2+}$ CATION RADICALS: ANION AND SOLVENT DEPENDENCE OF THE EPR SPECTRA.
K. Ichimori, H. Ohya-Nishiguchi and N. Hirota, Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan and K. Yamamoto, Institute for Physical and Chemical Research, Wako, Saitama 314, Japan

We have made a systematic investigation of the EPR spectra of the cation radicals generated by the electrochemical oxidation of $Co^{II}(tpp)$ (tpp:tetraphenylporphyrin) in different solvents and with different supporting electrolytes. The radical ion is identified as $[Co^{III}(tpp)]^{2+}XY$, where the coordinating ligands X and Y differ depending on the solvent and the supporting electrolyte. The coordinating power of the anion is: BF_4^-, $PF_4^- < NO_3^- < Br^-$, $Cl^- < CH_3COO^- < CN^-$ in accordance with the spectrochemical series. The EPR spectra strongly depend on the coordinating anions and the structures of the cation radicals in the solution were elucidated from the EPR spectra. The analysis of the hyperfine splittings and g-values lead to the following conclusions.
(1) The unpaired electron is mainly in the a_{2u} π orbital of the porphyrin skelton. (2) The small spin density on Co arises from the spin polarization of the metal-nitrogen σ bonds due to the spins on the nitrogen atoms.
(3) As the coordinating power of the anion increases, the spin densities on the nitrogen atoms increase. This result is rationalized in terms of a MO calculation which takes account of the effect of the coordinating anions.

144 DIPOLE-DIPOLE INTERACTION BETWEEN CUPRIC ION AND HUMAN MET-HEMOGLOBIN.
W. E. Antholine, Riccardo Basosi, and F. Taketa, Departments of Radiology and Biochemistry, Medical College of Wisconsin, 8701 Watertown Plank Road, Milwaukee, WI.

Human hemoglobin is known to have a high as well as a low affinity binding site for cupric ion on each of the constituent β chains. The copper that is bound to the low affinity site has been implicated in the selective oxidation of the β hemes. In the present work, analysis of epr spectra following the addition of four equivalents of cupric ion to unbuffered hemoglobin and immediate appropriate adjustment of the pH showed that two equivalents of cupric ion are bound to the high affinity binding site and two equivalents of copper are not detected. Because the met-heme iron signal is also reduced to about 50% of the expected value, it is suggested that the diminution in the signal of cupric ion is due to dipole-dipole broadening rather than to formation of cuprous ion. Corrections have been made for the more gradual reduction of the apparent intensity of high spin iron in the presence of excess cupric ion as described by Gurd (Gurd, et al., J. of Biol. Chem., 242, 5731-5735 (1967)) for the reduction of high spin iron from sperm whale ferrimyoglobin in the presence of several equivalents of cupric ion. The apparent diminution of the epr signals is attributed to the close proximity of the two paramagnetic ions; the copper binding site is deduced to be at or near the proximal histidines of the β chains.

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145 LOW FREQUENCY, S-BAND, EPR FOR CUPRIC BLEOMYCIN.

W. E. Antholine and J. S. Hyde, Department of Radiology, Medical College of Wisconsin 8701 Watertown Plank Road; D. H. Petering, Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, WI.

In contrast to previous S-band (3 GHz) data for cupric ion bound to hemoglobin or serum albumin, S-band spectra for bleomycin (^{65}CuBlm) in aqueous solvents which are poor glasses are poorly resolved for the $m_I = -1/2$ lines in the $g_{\parallel}$ region. Better resolved S-band spectra are obtained for CuBlm in a glass formed from mixing stochiometric amounts of Blm in dimethylsulfoxide with cupric ion in D_2O followed by dropwise addition of NaOD until a blue color has formed. The epr spectrum in this glass at -150°C is similar to the epr spectrum for CuBlm in D_2O at pH>5 except for improved resolution in the $g_{\perp}$ region and in the $g_{\parallel}$ region for the $m_I = -1/2$ line. The expanded region for the $m_I = -1/2$ line of the CuBlm spectrum clearly shows a symmetric pattern with an even number of lines. Simulation of the S-band spectra suggests four inequivalent nitrogen donor atoms, three with a_N = 10 Gauss and one with a_N = 15 Gauss. Thus S-band data not only indicate that four nitrogen donor atoms from Blm form the inplane coordination to cupric ion but that the contributions of the nitrogen donor atoms are inequivalent.

Supported by NIH grants CA-22184 and RR-01008 and funds from the University of Wisconsin-Milwaukee.

146 ELECTRON SPIN ECHO STUDIES OF SPIN-SPIN INTERACTIONS IN CYTOCHROME c OXIDASE. R. LoBrutto, G. Goodman and J. S. Leigh, Johnson Research Foundation/G4, University of Pennsylvania, 37th St. and Hamilton Walk, Philadelphia, PA 19104.

We have used the electron spin echo technique to measure a magnetic interaction between two of the four metal centers in isolated beef-heart cytochrome c oxidase. Specifically, we have found evidence of spin relaxation enhancement in the 'EPR visible copper' (Cu_A) by cytochrome a. In order to control for the effects of possible relaxation enhancement by cytochrome a_3 and by the 'EPR invisible copper' (Cu_B), both centers were reduced (to the Fe^{2+} and Cu^{1+} states, respectively), and the high-spin cytochrome a_3 iron was converted to low-spin form by the binding of carbon monoxide (CO). The effect of the cytochrome a iron on Cu_A was varied by the technique of redox titration. At a redox potential of 292 mV, both of these centers are fully oxidized, while the other two remain reduced. At 240 mV, the cytochrome a center is about half reduced, while Cu_A remains about 90% oxidized. T_1 values for both samples at 15°K were obtained by three-pulse (180°-90°-180°) echo measurements on Cu_A at g=2.03. No significant difference in T_1 was observed: T_1=21±3 usec at 292mV and 19±3 usec at 240 mV. However, preliminary T_2 measurements using a two-pulse (90°-180°) sequence have shown a small but significant effect. At 15°K and g=2.03, T_2=1.6±0.1 µsec at 240 mV and 1.2±0.1µsec at 292mV. By assuming a dipolar, $1/r^6$ type dependence of the interaction and by averaging over angular terms, it is possible to estimate based on this difference that the separation between the two centers is likbly to be between 12 and 20 Å.

147 EPR-DETECTABLE ACTIVE SITE DERIVATIVES OF THE COUPLED BINUCLEAR COPPER PROTEIN HEMOCYANIN. Dean E. Wilcox, William B. Mims and Edward I. Solomon. Department of Chemistry Stanford Universtiy, Stanford CA 94305 and Bell Laboratories, Murry Hill NJ 07974.

Hemocyanin, the oxygen carrying molecule of molluscs and arthropods, has an antiferromagnetically coupled and EPR silent binuclear cupric active site. A number of site derivatives which exhibit unique EPR signals, however, can be chemically prepared. We have conducted detailed studies of these EPR features in order to characterize the electronic and geometric structure of the active site. Met hemocyanin, like oxy, is an EPR silent binuclear cupric site derivative. Broad (0-5000 G) weak EPR signals, however, are associated with met and have been shown to orginate from ≤10% of the sites where the strong antiferromagnetic coupling can be reversibly eliminated. pH dependent competative displacement of the endogenous superexchange bridge by exogenous anions leads to a dipolar-coupled binuclear cupric site. Simulation of these EPR signals shows that exogenous bridging anions modify the Cu(II)-Cu(II) distance when the endogenous bridge has been removed. This behavior has allowed us to better characterize the endogenous protein bridge. Half met hemocyanin contains a Cu(II)-Cu(I) mixed valent site that shows very unusual EPR signals as the bridging exogenous anion is varied. For example, more complex parallel copper hyperfine patterns due to increased electron delocalization between the two coppers are found going down the halide series. We have used these anion perturbations and comparison to the mononuclear cupric met apo derivative to probe the half met electronic ground state. Orbital angular momentum of the ground state wavefunction as well as odd parity excited state mixing and contributions from ligands and the Cu(I) have been elucidated.

148 ESR STUDY OF INTRAMOLECULAR EXCHANGE OF METAL IONS IN ALTERDENTATE LIGANDS.

C. Daul, E. Deiss, J.N. Gex, D. Perret, D. Schaller and A. von Zelewsky
Institute of Inorganic Chemistry, CH-1700 Fribourg, Switzerland.

Planar vic-triketones, as e.g. ninhydrin or alloxan can be reduced to radical anions, which represent simple cases of alterdentate ligands (A. von Zelewsky, Inorg. Chem. **1981**, 20, 4448). In these cases, the ligands offer two equivalent chelating coordination sites and binding of a metal ion results in a species possessing a symmetric double minimum potential well on the energy surface (the two forms are enantiomers in two dimensional space). ESR spectroscopy is used to explore the pathway and the kinetics of exchange of metal ions between the two sites. As ions Mg, Ca, Zn, Cd (2+); Y, La (3+) are investigated. Those ions having a nuclear spin (67Zn; 111,113Cd; 89La; 139La) show that the exchange is intramolecular, because the metal hyperfine coupling is preserved in the case of rapid exchange. In many cases selectively broadened lines appear because the exchange rate is in the time range of ESR spectroscopy ($4 < \log(k*s) < 7$). Temperature dependent spectra yield the activation parameters of the intramolecular process. The spectra are fitted using the method developed by Heinzer (J. Mag. Res. **1974**, 13, 124). INDO calculations and a molecular mechanics model indicate an out of plane motion of the metal ion in the complex.

149 ANALYSIS AND INTERPRETATION OF EPR AND ZFR (ZERO-FIELD RESONANCE) OF Mn^{2+} IN TUTTON SALTS. S.J. Strach and R. Bramley, Research School of Chemistry, Australian National University, P.O. Box 4, Canberra, A.C.T. 2600, Australia.

ZFR analysis of Mn^{2+} contained in four Tutton salts has resulted in accurate determination of the most important spin Hamiltonian parameters (b_2^0, b_2^2, b_4^0; or D,E, (a+2F/3); $\underline{A}$ and $\underline{P}$). Combined with single crystal EPR studies we show that the few cases of positive b_2^0 in the literature are not substantiated or else are due to use of a different axis system from that used in cases with negative b_2^0. Moreover the consistent negative sign of this axial parameter can be associated with a compressed Mn-O bond in the distorted octahedral $[Mn(H_2O)_6]^{2+}$ unit. Analysis in terms of the superposition model shows that the intrinsic parameter b_2 is approximately -1300 MHz. The effects of changes in oxygen positions from the host structure locations and of water hydrogen atoms on the $\underline{D}$ tensor may both be important as shown by extended calculations using this model.

150 EPR OF Fe(III) IN SPODUMENE. ANALYSIS OF THE STRUCTURE DISTORTION AROUND Fe(III) BY MEANS OF THE SUPERPOSITION MODEL. J. M. Gaite, Laboratoire de Cristallographie (ERA 841) - UER Sciences, Université d'Orléans, 45046 Orléans Cedex, France.

The superposition model has been used to calculate the spin Hamiltonian constants of Fe(III) in spodumene ($LiAlSi_2O_6$). The calculations have been performed for second and fourth order constants. From the comparison between the calculated constants and the experimental ones, it is shown that the substitution of Fe(III) for Al(III) distorts the oxygen octahedron. The local structure around Fe(III) evoluate from the structure of spodumene towards the one of its isomorphic compound "iron spodumene" ($LiFeSi_2O_6$). It is also shown on the basis of this model that the oxygens of the octahedron M_1 are not all equivalent. The validity of the model is discussed; in our particular case only the nearest neighbors give significant contribution to the calculated constants.

There are several ways to describe the second and fourth order terms of the spin Hamiltonian, and different test may be built out to compare experimental and theoretical data. Some of them have been used and their significance is discussed.

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151 ESR OF HEAVY METAL DEFECTS IN ALKALI HALIDES AND APPLICATION TO COLOR CENTER LASERS.
D. Schoemaker, Physics Department, University of Antwerp (U.I.A.), B-2610 Wilrijk, Belgium

A large class of interesting defects can be produced by x-irradiation of alkali halides doped with the ns^2 (n=4,5,6) heavy metal ions Tl^+, In^+, Ga^+, Sn^{++}, and Pb^{++}. It includes centers as diverse as the np^3 negative ion centers Pb^- and Sn^- exhibiting static and dynamic Jahn-Teller effects and dimer centers such as a ⟨111⟩ oriented Tl_2^+. The latter molecule occupies a single cation site and is the manifestation of the interstitial Tl^0 atom. A particularly interesting set of defects are the so called laser active $M^0(1)$ centers $Tl^0(1)$, $In^0(1)$, and $Ga^0(1)$ (E. Goovaerts, J. Andriessen, S. V. Nistor, and D. Schoemaker, Phys. Rev. B 24, 29 (1981); W. van Puymbroeck, J. Andriessen, and D. Schoemaker, Phys. Rev. B 24, 2412 (1981)). In this center the M^0 atom is perturbed by a single anion vacancy. With $Tl^0(1)$ centers stable c.w. and modelocked picosecond pulse outputs of several hundred mW have been obtained at toom temperature in the 1.3 - 1.9 μm region (W. Gellerman, F. Luty, and C. R. Pollock, Opt. Comm. 39, 391 (1981); L. F. Mollenauer, N. D. Viera, and L. Szeto, Optics Letters 9, 414 (1982)). A survey of the more important properties of these centers will be given. In particular it will be shown that the mobility of the anion vacancy above 220K is essential for the production of most of these centers.

152 ELECTRON SPIN ECHO SPECTROSCOPY OF BIOLOGICAL MATERIALS. J. Peisach*# and W.B. Mims# *Albert Einstein College of Medicine, Bronx, NY 10461, #Bell Laboratories, Murray Hill, NJ 07974

Pulsed EPR techniques based on the generation of electron spin echoes have been shown to be a valuable tool in biological studies. Experiments have been of several types, the most useful, up to the present, consisting in the measurement of the electron spin echo decay envelope. This envelope is modulated by nuclear resonance frequencies, characteristic of the nuclei coupled to the electron spin. Its Fourier transform yields a nuclear superhyperfine spectrum associated with an EPR transition which is analogous to that obtained in an ENDOR experiment. Electron spin echo studies of biological materials can be used to establish the nature of a ligand bound to a paramagnetic metal ion. Thus, a measurement of the echo envelope spectrum can, in favorable cases, lead at once to the identification of histidyl imidazole nitrogen or some other metal ligand in a protein. Similar experiments can be performed whenever it is possible to modify a potential metal ligand by ^2H- or ^{13}C-substitution. Other studies can be used to demonstrate the presence of ^{23}Na, ^{31}P from phosphate, or ^2H, possibly from ^2H_2O, near a paramagnetic center. Information from these experiments is obtained from the appearance in the echo envelope of the appropriate nuclear modulating frequency, and from the depth and decay of the nuclear modulation pattern. In the case of weakly coupled nuclei, the depth of modulation is proportional to n/r^6 where r is the distance of the nucleus from the paramagnetic center and n is the number of equivalent nuclei. Several examples of such studies will be presented.

153 ACCESSIBILITY OF THE ACTIVE SITES IN METALLOPROTEINS TO SOLVENT AS DETERMINED BY ELECTRON SPIN ECHO ENVELOPE SPECTROSCOPY W. B. Mims&, J. Peisach&*, and J. L. Davis& &Bell Laboratories, Murray Hill, NJ 07974 *Albert Einstein College of Medicine, Bronx, NY 10461

We have measured 3-pulse electron spin echo envelopes for the copper proteins stellacyanin, azurin, and laccase, both before and after exchange against D_2O. By taking the ratio of envelopes we are able to separate out the modulation component due to these ^2H nuclei which take up positions in the vicinity of the active site after deuteration. A quantitative analysis of the modulation depth, based on a comparison with results obtained for partially deuterated Cu: aquo and Nd: aquo complexes, indicates that the sites in all three proteins are, in varying degrees, accessible to solvent. The nearest exchangeable water molecules in the electron transfer protein azurin appear to be considerably closer to the active site than was previously inferred from single crystal X-ray studies.

154 THE USE OF SWEPT-FREQUENCY EPR AT ZERO AND NON-ZERO APPLIED MAGNETIC FIELD S.J. Strach and R. Bramley, Research School of Chemistry, Australian National University, P.O. Box 4, Canberra, A.C.T. 2600, Australia.

Zero-field EPR (or ZFR) has several uses and advantages over conventional fixed frequency EPR and these will be discussed in general and with illustrative examples from our laboratory. Some of the advantages include improved accuracy through measurement of frequencies as opposed to fields and removal of errors of angular measurements. It will be shown that because of the inherent simplicity of the ZFR of non-magnetic transition ions, cases with several paramagnetic species or sites resulting in complex EPR spectra will benefit from a ZFR study and the technique has potential for applications in mineralogy and biology. The more general technique of swept-frequency EPR at a number of applied fields will also be discussed. This provides the best method of determining small 'off-diagonal' effects by directly observing the level repulsions (anti-crossings) which they cause.

155 ESR AT LOW FIELDS FOR NONINVASIVE DIAGNOSIS by Lawrence J. Berliner and Hiroyasu Nishikawa, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210, USA.

The application of ESR methods to the eventual imaging of in-vivo systems must overcome some different problems than those encountered in NMR. The two most obvious obstacles with common ESR configurations are the sample size in a resonant cavity arrangement and severe heating of aqueous samples at typical X-band frequency. Furthermore, any improvement upon these constraints above must not also compromise sensitivity in high dielectric media (such as H_2O). We report work with aqueous nitroxide spin labels at 1.85 GHz using coaxial propagation of microwave energy. After testing several helical, spiral and multi-turn flat coils as microwave coils, we have found that single turn flat "loops" of dimensions 0.7 - 1.0 cm diameter are optimum at this frequency. The sensitivity of these coils equals or exceeds that of an X-band ESR spectrum of a typical nitroxide (10^{-6} M). The (insulated) coils may be immersed in the aqueous solution with no detrimental effect.

156 Abstract not available.

157 CHEMISTRY AND STRUCTURE OF COALS: DIFFUSE REFLECTANCE INFRARED FOURIER TRANSFORM SPECTROSCOPY OF SURFACE REACTIONS, E. L. Fuller, Jr. and N. R. Smyrl, Oak Ridge Y-12 Plant*, Union Carbide Corporation, Nuclear Division, P. O. Box Y, Oak Ridge, Tennessee 37830

Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy is extremely useful in defining the chemical species present in the complex structure of coals and related materials.[1] The DRIFT technique has been shown to be surface sensitive and samples no more than a few microns, at most, of the surface of the solid carbonaceous solid. Problems of specular reflection and other factors will be addressed as related to theoretical and quantitative analyses of DRIFT spectra. The versatility of the technique is evident in comparative studies of natural samples ranging from living plant tissues, to woody structures, to lignitious and bituminous coals. Surface reactions are easily monitored by real-time in situ observation of such important reactions as hydration, oxidation, acetylation, etc. Detailed theory and mathematical analyses will be presented to lead to our quantitative analyses of these valuable and waning natural resources.

* Operated for the Department of Energy by Union Carbide Corporation, Nuclear Division, under U.S. Government Contract W-7405-eng-26.

[1] *Coal and Coal Products: Analytical Characterization Techniques*, E. L. Fuller, Jr., Editor, American Chemical Society, 1982.

158 THE CHARACTERIZATION OF SOOT BY FTIR AND OTEHR TECHNIQUES. M. S. Akhter, A. R. Chughtai, M. Cain, D. M. Smith, Department of Chemistry, University of Denver, Denver, CO 80208

Rocky Mountain Conference on Magnetic Resonance, Vol. 25 [1995], Iss. 1, Art. 1

The composition and surface structure of soot produced by hexane combustion have been examined by FT-IR and several other analytical techniques. The infrared studies have been made on the particulate, as collected from the flame, under a variety of conditions of temperature, pressure, and gaseous environments. Successive extraction of soluble components with a suite of solvents has been followed by GC, GC/MS, FT-IR, fluorescence, and NMR analysis of these extracts. From these studies and scanning electron micrographs, an understanding of the structure and reactivity of this material has emerged. A significant portion of the soot is estractable as polynuclear aromatic compounds, while the nonextractable solid structure with both aromatic and aliphatic portions contains such carbon-oxygen functionalities as acid anhydride, carbonyl and other linkages.

159 KINETICS OF THE REACTION OF NO_2 WITH SOOT. M. S. Akhter, A. R. Chughtai, and D. M. Smith, Department of Chemistry, University of Denver, Denver, CO 80208.

Qualitative and quantitative aspects of the reaction between NO_2/N_2O_4 and hexane soot have been studied by FT-IR. The rapid reaction near room temperature yields several surface species, including -C-NO_2 confirmed through reaction with $^{15}NO_2$ and $N^{18}O_2$. The dependence of the initial rate on the pressures of NO_2 and N_2O_4 obtained from treatment of the data using the Elovich equation has been obtained from the change in infrared band absorbance as a function of time as well as from separate manometric experiments. Plausible reaction mechanisms are discussed.

160 FT-IR STUDIES OF THE GAS PHASE REACTIONS OF OZONE WITH HYDRAZINE AND METHYL-SUBSTITUTED HYDRAZINES. E. C. Tuazon, W. P. L. Carter, A. M. Winer, R. Atkinson and J. N. Pitts, Jr., Statewide Air Pollution Research Center, University of California, Riverside, CA 92521.

The gas phase reactions of O_3 with hydrazine (N_2H_4), monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH), compounds which are in current use as rocket fuels, were investigated by in situ long pathlength FT-IR spectroscopy. The major products were: H_2O_2 and HN=NH from N_2H_4; CH_3OOH, CH_3NNH, HCHO, CH_2N_2 and H_2O_2 from MMH; and $(CH_3)_2NNO$ from UDMH. The reactions were studied at varying reactant ratios, in the presence and absence of radical traps, and in both air and N_2 atmospheres to yield information on the chemical mechanisms involved. Preliminary results on the reactions of O_3 with other methyl-substituted hydrazines will also be presented.

161 APPLICATIONS OF FTIR AND REACTION MODELING TO PROBLEMS OF INSTABILITY OF NO IN N_2 GAS MIXTURES. Barry C. Cadoff, National Bureau of Standards, Washington, DC 20234.

Standard Reference Materials (SRM's) which are certified and sold by the National Bureau of Standards, serve an important function in quality control procedures in the laboratory. One such SRM, NO in N_2 at the 1000 ppm level and packaged at 2000 psia in aluminum cylinders, is often used in environmental analyses. Particular care is taken to ensure the analytical accuracy and stability of SRM's. Occasionally, losses of about 1-3% in NO in N_2 mixtures are noted after a period of several months. A detailed investigation was carried out to examine the potential causes of this degradation in order to develop appropriate procedures for minimizing or preventing this problem. Stable and unstable cylinders containing NO in N_2 were included in this study. Potential common contaminants in these cylinders include O_2, NO_2 and H_2O. Kinetic data predicts that O_2 is rapidly converted to NO_2 by reaction with NO. Other reactive components, NO, NO_2 and H_2O, can enter into a series of reactions. These reactions, and the associated equilibrium constants, predict the formation, at equilibrium, of HONO and a smaller amount of N_2O_3. An FTIR spectrometer, equipped with a 100 meter effective path-length gas cell, showed the absence of N_2O_3 and only a small trace amount of HONO. Discussion will include the comparison of experimental results with predictions based on a homogeneous gas phase reaction model and the observations that support the proposed mechanism.

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162 IN SITU MEASUREMENT OF COMBUSTION GASES USING FOURIER TRANSFORM INFRARED (FT-IR) SPECTROMETRY.* L. R. Thorne and D. K. Ottesen, Sandia National Laboratories, Livermore CA 94550.

Recently we have used Fourier transform infrared (FT-IR) spectrometry to make in situ, non-perturbing measurements of the gases present during combustion. Both species concentration and temperature can be determined form the spectra. Absorption spectra in the 450 to 4000 cm^{-1} region are obtained by directing the focused output of the Michelson interferometer across a multi-element, diffusion flame burner onto a mercury cadmium telluride detector. The burner acts as a laminar flow reactor producing a hot, post-flame environment into which the fuel under investigation is injected. By raising o lowering the beam above the burner surface, data may be obtained for various extents of reaction with a time resolution of 10 ms. FT-IR absorption measurements for highly sooting, gaseous hydrocarbon flames and pulverized coal combustion will be presented to demonstrate the usefulness of these techniques in the study of particle-laden environments.

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* Work supported by the U. S. Department of Energy, DOE, under Contract DE-AC03-76DP00789.

163 FOURIER TRANSFORM INFRARED SPECTROSCOPY OF POLYMER INTERFACES. Jack L. Koenig, Department of Macromolecular Science, Case Western Reserve University, Cleveland Ohio 44106.

Fourier transform infrared spectroscopy has been used to characterize the polysiloxane adhesion promotors on glass surfaces. The nature of the chemical bonding to the glass has been investigated as well as the network structure of the coupling agent interphase. The role of deposition conditions has been studied including the concentration, temperature and time of treatment in the aqueous solution. These results will be reported and the molecular model generated will be discussed.

164 EFFECT OF CHLORIDE CONTAMINATION IN ACCELERATING PHOTODEGRADATION OF POLYMETHYMETHACRYLATE FILMS ON SILVER SURFACES. J. D. Webb, J. R. Pitts, T. M. Thomas, P. Schissel, and A. W. Czanderna.

The rate of photodegradation of polymethylmethacrylate (PMMA) on clean silver, as measured using FTIR-RA spectroscopy, is slow under 10X terrestrial UV illumination (wavelengths longer than 285 nm). However, the rate of photodegradation is accelerated substantially when the silver substrates are contaminated with chloride ions. Silver surfaces rapidly accumulate an insoluble chloride layer when exposed to aqueous chloride solutions, gaseous chlorine or gaseous hydrogen chloride.

Evidence for the accelerated photodegradation of PMMA on chloride-contaminate silver, which resulted in visual darkening of the samples, will be presented. IR-RA spectra of the samples taken before and after 1 h UV exposure reveal accumulation of some carbonyl at 1750 cm^{-1}, extensive loss of the PMMA carbonyl at 1731 cm^{-1}, and some loss of ester functionality from 1100 to 1300 cm^{-1}. There is also a general decrease in specularity of the samples. Other IR-RA spectra taken during the experiments reveal that most of the changes occur during the first fifteen minutes of UV exposure. Chlorine concentrations of up to 14 atomic per cent were determined from XPS spectra of the silver surfaces after exposure, removal of the PMMA film by solvent stripping, and argon ion etching.

From these observations, it is thought that the PMMA layer is photocatalytically altered by the silver chloride interfacial layer, and finely-divided silver is deposited at the interface.

...FILM DEGRADATION MECHANISMS. C. Sergides, J. Hashim, A. R. Chughtai, and D. M. Smith, Department of Chemistry, University of Denver, Denver, CO 80208. *Rocky Mountain Conference on Magnetic Resonance, vol. 25 (1983), Abs. 180.*

An FTIR technique for the study of polymer film photodegradation* has been employed to elucidate the mechanisms involved in the photodegradation of BPA-polycarbonate a polyacrylonitrite. Experiments in the presence of air and in inert atmospheres, involving sharp cut-off filtering of the radiation source, and with polymers isotopically substituted with ^{18}O and ^{2}D have revealed the degradative pathways involved in both polymers. This technique is a powerful direct approach to the study of the molecular events involved in the degradation of surface films.

*J. D. Webb, P. Schissel, A. W. Czanderna, A. R. Chughtai, and D. M. Smith Appl. Spectrosc. 35, 598-603 (1981).

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FTIR AS AN ANALYTICAL TOOL IN A POLYMER LABORATORY
Louis M. DiBello, Cryovac Div.; W.R. Grace & Co.,
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The FTIR has proven to be an invaluable analytical tool in the polymer laboratory. Analytical techniques have been developed which makes use of the repeatability and speed of the FTIR to decrease analysis time of additives in polymers from 48 hours to times of 1 hour for direct measurements of a resin to a time of 25 hours when extraction of the additives are required. These time forms are beneficial to quality control laboratories of our manufacturing facilities. This paper will detail a method of analysis for % vinyl acetate in ethylene-vinyl acetate copolymers versus the pyrolysis method, a direct measurement of a slip additive in a polyolefin and an extraction of various additives (antioxidant and two slip agents) from a polyolefin followed by a multi component analysis. These methods will detail the making of analytical standards, calibration of the instruments (a Nicolet 7199 and a Nicolet MX-1), program writing of the method, repeatability and accuracy, and the transition of the methods to a quality control laboratory.

167 *Abstract not available.*

168 THERMAL DECOMPOSITION OF ENERGETIC MATERIALS BY RAPID-SCAN FT-IR. Thomas B. Brill and Richard J. Karpowicz, Department of Chemistry, University of Delaware, Newark, Delaware 19711.

The chemical and physical changes taking place in the solid phase of a rapidly decomposing material are among the more challenging and unexplored frontiers in materials science. The solid and melt form an unstable heterogeneous mixture containing simultaneous reactions. The thermal decomposition of energetic solids are particularly intriguing owing to the vigorous changes that take place. In these compounds the condensed base chemistry plays an important role in the thermal behavior. Few time-resolved spectroscopic methods are available to study the condensed phase processes. However, rapid-scan FT-IR in which sequential IR spectra can be recorded every 20 msec provides a promising approach. High heating rates can be produced by resistance heating or by a CO_2 laser. The pressure can be variable. The application of these techniques is underway to detect early decomposition products in the nitramines, octahydro-1,3,5,7-tetranitro-1,5,7-tetrazocine (HMX), hexahydro-1,3,5-trinitro-s-triazine (RDX) and an azide derivative of HMX. Previously undetected HN_3 from azide complex is observed in the initial sec of heating and diminishes in concentration after this time.

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169 DIFFUSE REFLECTANCE FT-IR SPECTROMETRY: A POWERFUL TOOL FOR [illegible] SAMPLES. Peter R. Griffiths, Department of Chemistry, University of California, Riverside, CA 92521. [illegible] al.: 25th RMC

Since we first described an optical configuration for high sensitivity diffuse reflectance FT-IR spectrometry in 1978, this technique has become remarkably popular. Spectra can now be measured with a sufficiently high signal-to-noise ratio that advanced data processing routines, such as Fourier self-deconvolution and factor analysis, may be applied. In this talk, diffuse reflectance spectrometry of coals, adsorbed species and proteins will be discussed. A heatable, evacuable cell for investigating gas-solid reactions will be described, and its performance will be illustrated through deconvolved spectra of coals subjected to air oxidation. The behavior of the diffuse reflectance of coals as they are diluted in KCl is interesting, and leads to a novel method for the analysis of mineral matter in intact coals. Spectra of CO on supported metal catalysts can be measured down to coverages of 10^{-3} monolayers, and sometimes less. We will demonstrate the possibility of monitoring industrially significant reactions occurring at high temperature and high gas pressure. Finally an unusual method for determining the conformation of solid proteins will be shown.

170 DILEMMA: TRANSMISSION, ATR, DRIFTS OR PAS STUDIES BY FT-IR? John Graham and W. G. Fateley, Chemistry Department, Kansas State University, Manhattan, KS 66506. John Casper, IBM Instruments, Inc., Danbury, CT 06810.

In order to obtain the best possible FT-IR spectrum of a sample, one is faced with the choice of several sampling techniques: Transmission through the sample, attenuated total reflection of the sample, diffused reflection or DRIFTS from the sample, or Photoacoustic studies of the material. A discussion will be presented on which FT-IR technique works best for specific sample problems. A discussion of the advantages and disadvantages of all techniques will be reviewed.

171 PRECISION BETTER THAN 1 MHz IN FOURIER SPECTROSCOPY BELOW 1000 CM^{-1}
J. Kauppinen, V-M. Horneman, and E. Kyrö, University of Oulu, Finland

Fourier transform spectrometer (1, 2, 3) at the University of Oulu is working with a resolution of ~0.0045 cm^{-1} and a very high wavenumber precision of ~$\pm 3\times10^{-5}$ cm^{-1} (1MHz) below 1200 cm^{-1}. The latest modifications of this instrument are a dynamic alignment system (4) of the interferometer and an adjustable frame of the beam splitter. In addition, the development of computation of line positions is very important in order to achieve high precision. As a calibration standard (5) we use the pure rotational lines of H_2O, the ν_2 band of CO_2, and the ν_1 band of OCS which were simultaneously recorded by our instrument. The wavenumber scale of this spectrum was fixed with the help of seven OCS lines measured by a heterodyne frequency technique (6).

(1) J. Kauppinen, Appl. Opt. 14, 1987 (1975)
(2) J. Kauppinen, Acta Univ. Oulu A 38, (1975)
(3) J. Kauppinen, Appl. Opt. 18, 1788 (1979)
(4) J. Kauppinen and V-M. Horneman, "Research Reports in Optics", in Proceedings, Symposium of Optics, 23 Nov. 1981, Helsinki U. Technology, Finland
(5) J. Kauppinen, K. Jolma, and V-M. Horneman, Appl. Opt. 21, 3332 (1982)
(6) J.S. Wells, F.R. Petersen, A.G. Maki and D.J. Sukle, Appl. Opt. 20, 1676 (1981)

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172 USE OF FTIR AS A GENERAL LABORATORY SUPPORT INSTRUMENT. Wayne Wasson, AFWL/SUE Kirtland AFB, NM, 87117.

Fourier Transform Infrared Spectroscopy (FTIR) has advantages for general laboratory support in preference to grating spectrometers. For most purposes, FTIR is faster, more sensitive and can use methodologies not possible with grating spectrometers. These advantages are well documented for analytical chemical measurements. However, they are not well documented for another primary use of FTIR involving the measurement of optical properties. FTIR is specifically superior for the measurement of spectral reflectivities and specifically inferior for the measurement of spectral transmittivity. The factors of photometric accuracy, throughput stability and beam geometry must be considered when using FTIR for precise optical measurements. The use of optical standards must be carefully considered and correlated to instrumental function. The utilizations of variable polarizers offers a unique advantage in FTIR if the instrument is used in a single beam configuration. In summary, the analysis of solids, liquids, and gases and the measurement of optical properties make FTIR an indispensable instrument for general laboratory support.

173 AN FT-IR IN THE OPEN LAB CONCEPT,
J. W. Ryan, BFGoodrich Company, P. O. Box 122, Avon Lake, Ohio 44012

During 1976 the growth in demand for infrared staff support to R&D, Manufacturing and Marketing groups began to accelerate noticeably. To meet this growing demand a few selected scientists were encouraged to use either of two dispersive IR's available to solve simpler problems of compound identity. Early in 1981 a small low-cost FT-IR system was purchased to replace one of the dispersive instruments.

In order to establish maximum utilization of the FT-IR, it was situated in an open lab and an infrared training program was made available at frequent intervals to interested Goodrich personnel. The facile operation of the push-button FT-IR has encouraged a large percentage of people who have completed the IR course to use the instrument to help solve their own problems. In the most recent nine month period 33 people have used the instrument for an average of 3 hours a day.

Work by the newly trained operators is generally limited to quality checks, where limited interpretative skills are required. For unknowns or unusual occurrances, staff spectroscopists are available for help. Some operators are developing skills to perform more complicated tasks such as spectral subtractions using stored reference spectra.

The results to date are most encouraging. Several examples of successful results of this open lab concept will be discussed.

174 METHODS OF ANALYSIS OF TABLET CONTENTS BY FTIR. David C. Peters (Analect Instruments, 1231 Hart Street, Utica, NY 13502) and J. William Mohar (Analect Instruments, 1731 Reynolds Avenue, Irvine, CA 92714).

In fifteen years, Fourier Transform Infrared Spectrometers have developed from technological marvels with exorbitant prices into dependable, practical instruments. This dramatic price reduction has opened new markets to FTIR's power and sampling flexibility. Indeed, the instruments have migrated from corporate and academic research centers into routine quality control and quality assurance labs. In contrast to the research lab where unique, recalcitrant materials are analyzed, the QC lab repetitively analyzes a sample of goods produced or received; once sampling conditions are optimized, the procedure is routine. This environment requires high sample throughput, minimal sample preparation and essentially automated performance and data reduction. In the pharmaceutical industry, for example, careful quality control is imperative for consumer and corporate protection. This paper will survey recent developments in qualitative and multicomponent quantitative analyses of tablet contents by Analect FTIR. Sampling methods discussed will involve specular and diffuse reflectance, and photo acoustic spectroscopy.

175 SOME USES OF INFRARED PHOTOTHERMAL BEAM DEFLECTION SPECTROSCOPY. M.J.D. LOW, Department of Chemistry, New York University, New York, N.Y. 10003.

IR photothermal beam deflection spectroscopy (PBDS) of solids is described. It is an offshoot of photoacoustic spectroscopy (PAS) and involves heating a surface by the photothermal effect, but differs from PAS in the way that the heating of the gas above the solid's surface is detected. With PAS a microphone is used so that the sample is usually confined in a very small cell also containing the detector. With PBDS, the refractive index gradient in the gas caused by heating is detected by observing the deflection of a laser beam grazing the solid's surface, so that sample cells per se are not needed, and the size limitation on samples is removed. Portions of the surfaces which are truly massive can thus be examined. Also, if a sample must be kept in a cell, as is required for surface studies, the surface can be examined under controlled conditions, and without potential contamination by the detector, because the detection system is outside the cell. Examples of IR spectra including those of massive samples, a variety of organic and inorganic solids and of carbons are given. PBDS is also especially useful for surface studies of materials which scatter and/or absorb so greatly that conventional IR transmission methods are impossible. Examples are given of spectra of surface species on carbons, carbon-supported metal catalysts, and on silica below 1200 cm^{-1}.

176 THE STUDY OF OXIDE FILMS ON METALS USING FT-IR REFLECTANCE SPECTROSCOPY*
D. K. Ottesen, L. R. Thorne, and A. S. Nagelberg; Sandia National Laboratories, Livermore CA 94550.

Fourier transform infrared (FT-IR) reflectance spectroscopy has been developed in our laboratory as a sensitive analytical technique for the characterization of thin, non-metalic films on metalic substrates. Our efforts have been directed primarily at understanding the oxidation of ferrous alloys commonly used in corrosive environments; however, the methods developed apply, in general, to dielectric films on metalic surfaces. Our experimental data consist of specular reflectance measurements at various angles of incidence and beam polarizations. These results will be presented along with theoretical calculations of infrared reflectance for multi-layered films. These calculations take into account the state of polarization of the light, the variable angle of incidence due to beam divergence and light scattering due to surface roughness. The fit of the theoretical spectra to the measured data is very good for many of the systems we have investigated. Since the calculated spectra are very sensitive to the structure of the film, the close agreement with the observed spectra provides strong evidence for the order in which the layers overlay the metal surface as well as the composition and thickness of each layer.

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177 AN INFRARED AND EPR STUDY OF IMPURE ZINC OXIDE. D. L. Gladstone, A. R. Chughtai, and D. M. Smith, Department of Chemistry, University of Denver, Denver, CO 80208.

Infrared absorption bands are observed in the 2200-1700 cm^{-1} region when gases such as oxygen and chlorine are adsorbed on zinc oxide powder prepared by the thermal decomposition in vacuo of zinc oxalate (1). These bands, not present following the decomposition process, are related to impurities in the zinc oxide. EPR studies have shown a decrease in unpaired electrons and their shift to a more hindered environment with adsorption of oxygen on the surface. These data and infrared studies suggest a mechanism in which the adsorption of electron withdrawing gases brings about the formation of bonds between the impurity atoms and oxygen of the zinc oxide lattice.

1. D. M. Smith and R. P. Eischens, J. Phys. Chem. Solids 28, 2135-2142 (1967).

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178 AQUEOUS REVERSE PHASE LC/FT-IR DEVELOPMENTS AND APPLICATIONS. K.S. Kalasinsky, J.T. McDonald and V.F. Kalasinsky, Mississippi State Chemical Laboratory, P.O. Box CR, Mississippi State, MS 39762 and Mississippi State University, Chemistry Department, Mississippi State, MS 39762

Previously, there have been two main techniques for LC/FT-IR, one employing a flow-through cell, and the other utilizing a solvent elimination system with subsequent analysis of the solute by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. A modification of the DRIFT technique for HPLC eluent analysis has been accomplished. For aqueous reverse phase LC/FT-IR the removal of water from the solvent system is imperative as any H_2O present in the sample not only degrades the infrared halide salt substrate, but also exhibits strong absorption bands in the infrared spectrum. To address the problem of water elimination, an acid catalyzed reaction with a water-specific reagent is used. The products of the reaction are organic compounds which are readily volatilized and removed in the sample concentrater. Infrared analysis indicates that no water is present in the final drops that are placed on the salt substrate. This system has several inherent advantages over the previous designs. Its size is compact enough to fit into a standard sampling compartment without major modifications. It is readily applicable to "on-the-fly" systems with FT-IR analysis and can also be used as an external sampling technique for dispersive infrared systems. This is made possible by all of the liquid chromatograph eluent being deposited on the substrate "train" and "stored" for analysis. This also allows for signal averaging of a particular fraction of interest and also for the recovery of this fraction for alternate analysis.

179 AN HPLC-FTIR INTERFACE WITH SUBMICROGRAM DETECTION LIMITS FOR BOTH REVERSE PHASE AND NORMAL PHASE CHROMATOGRAPHY. Pamela J. Duff, USA Ballistic Research Laboratory, DRDAR-BLI, Aberdeen Proving Ground, MD 21005 and Peter R. Griffiths, University of California at Riverside, Riverside, CA 92521

One approach for interfacing LC-FTIR is the solvent elimination technique described by D. Kuehl and P.R. Griffiths (Anal. Chem., Vol. 52, p. 1394, 1980). The effluent from a liquid chromatograph is concentrated prior to deposition onto KCl and measurement of the spectrum by diffuse reflectance infrared FT-IR (DRIFT). However, this system is not compatible with the aqueous solvents used in reverse phase chromatography. To rectify this problem, a system has been developed in which samples are extracted on-line from the aqueous mobile phase into dichloromethane and then concentrated and deposited onto KCl for measurement by DRIFT. The design of the concentrator and the manner in which the sample is deposited is critical to obtaining good quality IR spectra. In this system, the concentration factor can be easily controlled and there is no loss of thermally labile or volatile components. Submicrogram detection limits are easily achieved for samples which elute at 80% methanol or less (to ensure immiscibility of the dichloromethane and the aqueous phase) and for which at least 15% of the injected amount extracts into dichloromethane. If these conditions are not met, water can also be added on-line to the column effluent to effect phase separation, or modifiers can be added to facilitate extraction. Examples of compounds recovered after simple extraction with dichloromethane and those requiring addition of a modifier will be presented. Applicability to ion suppression and ion-pairing chromatography will also be demonstrated.

180 ISOLATION AND MOLECULAR IDENTIFICATION OF ULTRAMICRO CONTAMINANTS BY FOURIER TRANSFORM INFRARED SPECTROSCOPY, Merlin E. Lacy, Rockwell International, Anaheim, CA 92803

Most nonmetallic contaminants previously regarded as too minute for chemical analysis may now be identified by ultramicro Fourier transform infrared spectroscopy (FTIR). The detectability limit for this procedure is approximately one nanogram.

The technical features of FTIR which make possible such performance will be described. Also, the use of microtools and microscopy in sample isolation and mounting will be outlined.

Ultramicro FTIR permits the nondestructive molecular identification of individual contaminants. Unlike many conventional analytical procedures, it is not necessary to rely upon analysis of residue obtained from rinsing procedures in which the presence of extraneous materials often obscures the results.

Several case histories will be presented which demonstrate the usefulness of this procedure in solving contamination problems in guidance system and microelectronic applications.

181 A RAPID METHOD FOR DETERMINATION OF NITROSOAMINE FORMED FROM RHODAMINE DYE AND NITRITE ION IN RIVER WATER. S. M. Johnson and T. R. Steinheimer, U. S. Geological Survey, P.O. Box 25046, Mail Stop 407, Denver Federal Center, Denver, Colorado 80225.

Rhodamine dyes are anionic xanthene derivatives that are used extensively as water-tracing agents in environmental and pollution investigations. One of their hydrolysis products, diethylamine, is known to react with nitrite ion in surface waters to form N,N-diethyl-N-nitrosoamine (DENA), a potent mammalian carcinogen. The potential for this reaction to occur in South Platte River water has been examined. A rapid procedure for the determination of DENA in river water has been developed. The method involves solid-phase extraction followed by gas chromatography with a nitrogen-selective detector. The technique permits reliable DENA determination to be completed in less than 2-1/2 h. Minimum detectability is less than 0.5 µg/L and recoveries for laboratory-fortified samples averaged greater than 50%. Instrumental analysis is fully automated from sample injection through chromatographic data review and quantitative calculation. Known quantities of DENA were added to 10% of the samples throughout the study in order to verify recoveries. Solid-phase extraction is an efficient alternative to classical liquid-liquid partition for removal of organic residues from water. This approach offers several advantages including selectivity and speed. In addition, the convenience attendant to smaller solvent volumes, freedom from emulsions, decreased glassware needs, and fewer method-blank associated problems, makes this technique amenable to field sampling.

182 FLUORESCENCE SPECTROSCOPY APPLIED TO THE INTERPRETATION OF FULVIC ACID BONDING TO COPPER IN AQUEOUS SYSTEMS, Marvin C. Goldberg, U.S. Geological Survey, P.O. Box 25046 MS 424 Denver Federal Center, Lakewood, Colorado 80225

Quenching of fulvic acid fluorescence due to copper bonding indicates both specific and non-specific bonding mechanisms. Fulvic acid solutions at pH 4.2, 5.0, 6.0 and 7.5 were titrated with copper chloride, both with and without competing electrolytes (potassium chloride and calcium chloride). In the presence of competing electrolytes, more copper is required to quench the fluoresence. The effect is strongest above pH 6.0. Around pH 7.5, however, the molecular structure of fulvic acid changes and interpretation of the data becomes less reliable. The results indicate that copper first bonds specifically to fulvic acid. When the specific sites are filled, the molecule still carries a net negative charge and additional copper can be non-specifically bound. Non-specific bonding is weaker but can accomodate many more cations than specific bonding. If a competing cation, such as potassium or calcium, is present, the amount of specifically bound copper is reduced according to the displacement strength of the competing cation.

183 PHOTOLYSIS OF DIOLS IN AQUEOUS SYSTEMS. Kirkwood M. Cunningham and Marvin C. Goldberg, U. S. Geological Survey, P.O. Box 25046 MS 424 Denver Federal Center, Lakewood, CO. 80225

The photochemistry of the simplest diol, ethylene glycol, was studied in aqueous suspensions of goethite, (FeOOH), at neutral pH, in the wavelength range 300-400 nm. In the absence of goethite, there is no photoreaction of glycol. In the presence of goethite, glycol is oxidized to formaldehyde. The quantum yield of formaldehyde formation ranges from 2 x 10^{-4} at 0.2 M glycol, to 8 x 10^{-4} at 2.0 M glycol. The quantum yield extrapolated to zero glycol concentration is 1.7 x 10^{-4}. These results indicate that the photoreaction proceeds by two mechanisms, one independent and one dependent on glycol concentration. The known photochemistry of the Fe^{+3} - ethylene glycol system in acid solution suggests that:

1. the concentration independent reaction is the photoreduction of goethite Fe^{+3} to Fe^{+2}, with the release into solution of a hydroxyl radical which then reacts with a glycol molecule.
2. the concentration dependent reaction is the abstraction of an electron from glycol sorbed on the goethite surface which reduces lattice Fe^{+3} to Fe^{+2}.

These results point out photochemical reactions that can take place on the surfaces of iron hydroxide particles in aquatic environments.

184 REVIEW OF LIGHT SCATTERING TECHNIQUES FOR PARTICLE SIZE AND MASS MEASUREMENTS IN AQUEOUS SYSTEMS Marvin C. Goldberg, Eugene R. Weiner, and Kirkwood M. Cunningham U. S. Geological Survey, P.O. Box 25046 MS 424, Denver Federal Center, Lakewood, CO 80225

Timely, accurate data on particle size and mass concentration of suspended sediment in natural water bodies is of extensive value. There seems to be a dearth of commercial instrumentation at the present time for producing this measurement on-site and continuously. Technologies which might be used for this purpose include: light obscuration, light scattering, holography, sedimentation (including elutriation and settling), turbidimetry, x-ray absorption, acoustic absorption, and gamma and beta absorption. Of these, light scattering is the most promising phenomenon that can be used to produce a sediment measurement device that is capable of size measurements ranging from <1 to 1000 microns and concentration measurements ranging from 50 to 10,000 ppm (and up to 400,000 ppm by dilution methods). One such device developed in our laboratories uses laser light backscattered at angles greater than 160°. It can operate in a rapid batch mode and meet the criteria cited.

185 GROUND-WATER CONTAMINATION BY HAZARDOUS CHEMICAL COMPOUNDS DERIVED FROM WOOD-TREATMENT PROCESSES. W. E. Pereira and C. E. Rostad. U.S. Geological Survey, P.O. Box 25046, MS 407, Denver Federal Center, Denver, Colorado 80225.

Hazardous waste materials produced during wood-treatment processes were stored in surface impoundments near Pensacola, Florida. Leakage from these impoundments has resulted in ground-water contamination of one of the major sand and gravel aquifers in northwest Florida. This aquifer discharges into Pensacola Bay; therefore, there is potential for contamination of the bay and possible harmful effects on the marine ecology. Investigations to assess the areal extent of ground-water contamination and the presence of these wastes in the bay are currently in progress. Studies of the physical, chemical, and biological processes controlling the fate and movement of the wastes in the ground water indicate that numerous complex reactions are occurring both in ground water and in bottom material in the impoundments. Bottom-material samples from an overflow pond were analyzed for organic compounds, and ground-water samples were analyzed for organic and inorganic constituents. Organic compounds were isolated by solvent extraction or sorbent-trace enrichment techniques and characterized by gas chromatography, mass spectrometry. Trace elements were determined by emission spectroscopy and major anions by standard procedures. Bottom-material samples contained alkylated and chlorinated phenols, polychlorinated dibenzodioxins, polycyclic aromatic hydrocarbons, and azaarenes. Ground-water samples contained significant concentrations of cadmium, iron, arsenic, and cyanide, and several organic compounds that were present in the initial waste liquors. Several oxygenated derivatives of polycyclic aromatic hydrocarbons and azaarenes also were identified in the ground water. The origin and fate of these compounds will be discussed.

186 PARTITIONING OF POLYCYCLIC COAL-TAR CONSTITUENTS IN A TWO-PHASE, GROUND-WATER SYSTEM. C.E. Rostad and W.E. Pereira. U.S. Geological Survey, P.O. Box 25046, Mail Stop 407, Denver Federal Center, Denver, Colorado 80225.

As part of an ongoing investigation of the fate and movement of organic compounds derived from coal-tar wastes in a contaminated aquifer in St. Louis Park, Minnesota, a study was made to determine if the octanol-water partition coefficients of various polycyclic aromatic compounds could be used to predict the partitioning of these compounds in a tar-water system. Coal tar contains numerous polycyclic aromatic compounds, many of which are suspected carcinogens and mutagens. Partitioning of hazardous compounds from the organic phase into the aqueous phase may pose an environmental health hazard in nearby public water supply wells. Fluid from this aquifer develops two phases upon settling: an upper aqueous phase and a lower, oily tar phase. Thirty-one selected polycyclic aromatic compounds were quantified in the separate phases using gas chromatography, mass spectrometry techniques. The compounds chosen were from four different classes: 8 nitrogen heterocycles, 5 sulfur heterocycles, 5 oxygen heterocycles, and 13 polycyclic aromatic hydrocarbons. Tar-water partition coefficients of these compounds were calculated and compared to their octanol-water partition coefficients reported in the literature. Within each compound class, the tar-water values of the higher molecular-weight compounds were similar to the reported octanol-water values. However, the tar-water values for the lower molecular-weight compounds studied in each class were consistently much greater than the literature octanol-water values. The decreased concentration in the aqueous phase of these more water-soluble compounds may be due to microbial or chemical transformation. Octanol-water partition coefficients are useful as an indication of coal-tar compound partitioning in a two-phase, tar-water system, provided other possible effects such as absorption and biodegradation also are considered.

187 APPLICATIONS OF SEMI-MICRO HPLC TO ENVIRONMENTAL ANALYSIS
S. Michael McCown, Beckman/Altex 1780 Fourth St. Berkeley, CA 94710

HPLC finds comparatively limited use in environmental analysis. Modern semi-micro columns, coupled with scanning UV-Vis. absorbance detection, present the means of overcoming the two most often mentioned objections to the technique: sensitivity, and selectivity

Pesticide residues and metabolites, herbicide residues and phthalate esters, as well as polynuclear aromatics, exhibit greatly improved limits of detection and significantly increased selectivity with the use of this technique. Method development and verification times are reduced, as is solvent consumption. Details of selected applications of the technique in water and air pollution and personal exposure monitoring will be presented.

188 APPLICATIONS OF SHORT ALKYL CHAIN, WIDE PORE, REVERSE PHASE PACKING IN HPLC

Margaret May-Sheng Chan & J. S. Hobbs - Beckman/Altex
1780 Fourth St. Berkeley, CA 94710

The introduction of wide pore chemically bonded, silica packings for high performance liquid chromatography has opened up new areas of application for the technique. In particular, the separation of proteins and peptides has become a rapid, reliable technique with separations taking minutes where they previously took hours. In addition to examples of high speed protein analysis, applications in other areas, including nucleic acids and industrial polymers, will be demonstrated.

189 HIGH SPEED LIQUID CHROMATOGRAPHIC ANALYSIS OF SYNTHETIC DYES

J. P. Chaytor, R. Heal - Beckman/Altex Technical Center
Milton Keynes - England John S. Hobbs - Beckman/Altex
1780 Fourth St. Berkeley, CA 94710

The use of synthetic dyes is widespread in the food, pharmaceutical and cosmetic industries. A rapid separation of the common dyes using a high speed, 3μ particle, reverse-phase column will be demonstrated together with multiwavelength monitoring to aid in peak identification. The use of on line scanning to confirm identity will also be illustrated.

190 HPLC ANALYSIS OF 2-(5-CYANOTETRAZOLATO)PENTAMMINE COBALT (III) PERCHLORATE (CP) ON A POLYAMIDE COLUMN; Roy J. Schumacher, *Monsanto Research Corporation*, Mound Plant, Miamisburg, Ohio 45342.

2-(5-Cyanotetrazolato)pentammine cobalt (III) perchlorate (CP) was determined to have properties that would make it useful as a deflagration-to-detonation explosive. CP amide 2-(5-carboxamidotetrazolatopentammine) cobalt (III) perchlorate, as the major preparation by-product, gave the CP undesirable firing characteristics above a certain level.

A HP LC method was developed to analyze for this impurity utilizing a polyamide column to quantitate the amide in chromatographic runs requiring less than 15 minutes each. Though the polyamide is not a high surface area material, having a surface area of only 21 m^2/gr and producing columns of less than 200 plates per meter, an α value of 4.6 was obtained. This results in a separation of CP from CP amide showing baseline resolution on a short, 15 cm column. The detection limit is less than 80 ng of amide. The amide content shows a standard deviation of less than 0.1%. The detection response is linear up to 4 μg of amide.

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KINETICS OF THE OXIDATION OF SUBSTITUTED FERROCENES AT PLATINUM AND InP ELECTRODES. **Robin L. A. Pravata and Carl A. Koval. *University of* Colorado, Chemistry Department, Campus Box 215, Boulder, CO 80309.**

We have measured the formal reduction potentials and heterogeneous rate constants for the oxidation of a series of substituted ferrocenes at platinum electrodes in acetonitrile. The reduction potentials span a range of over one volt. Despite spanning a large range in reduction potentials, the substituted ferrocenes have similar structures, and the redox couples all involve a one-electron oxidation to form a monocation. The homogeneous self-exchange rate constants for the ferrocenes are similar, as are the heterogeneous rate constants.

The reduction potential range of the series of substituted ferrocenes spans the band gap of InP, therefore, it is an excellent kinetic probe for the systematic study of semiconductor/solution charge transfer processes. We have measured dark currents at InP under conditions of accumulation, depletion, and inversion. The magnitude and potential dependence of these currents allow us to test certain predictions about the nature of the semiconductor/solution interface.

192 SOLID SORBENT SAMPLING OF SULFUR DIOXIDE IN WORKPLACE ATMOSPHERES. Knut Irgum and Mats Lindgren, Department of Analytical Chemistry, University of Umea, S-901 87 Umea, Sweden.

For personal monitoring of sulfur dioxide in workplace atmospheres, a solid sorbent sampling tube has been developed. The air to be tested is drawn through the tube and stabilization of the sampled sulfur dioxide is accomplished by reacting the hydrolyzed gas wity glyoxal-hydrate, yielding a stable addition compound. For pH control a partly regenerated acrylic acid type weak cation exchanger (pk_a = 5.1) was used as support for the reagents.

The α-hydroxy-sulfonic acid formed is desorbed in carbonate eluent or water and quantified by ion chromatography or a modified pararosaniline method. Excellent recoveries of SO_2 were obtained from laboratory test atmospheres at different relative humidities ranging from 5 to 90% RH. Recovery after one week of storage after sampling was still more than 90%. Working range for the overall method using pararosaniline detection is from 0.1 to 10 times the Treshold Limit Value for sulfur dioxide when using a 15 min sample drawn at 200 ml min^{-1}.

193 MICROCOMPUTER BASED DATA ACQUISITION AND REDUCTION SYSTEM FOR ION CHROMATOGRAPHY, Randall K. Stahlhut, Susan R. Bachman, Illinois State Water Survey, Champaign, IL 61820-9050

A Dionex Model 12 ion chromatograph equipped with an autosampler, a high resolution analog to digital (A/D) converter, and an APPLE II microcomputer have been combined to form an automated data collection and analysis system for measuring chloride, orthophosphate, nitrate, and sulfate in rainwater. A computer program was developed which inputs all data from the A/D converter, generates plots on the high resolution graphics screen, and stores it in the computer memory. At the end of the sampling period, data are stored on a 5 1/4 inch floppy disk and processed. The end result is a cost effective 'near' real time ion chromatographic analysis system requiring approximately fourteen minutes per sample. Detection limits and accuracies have been determined using replicate analyses of numerous standard solutions and precipitation samples.

194 USE OF A DIGITAL RECORDER FOR DATA ACQUISITION AND REDUCTION IN THERMAL ANALYSIS, J. R. Delmastro, Exxon Nuclear Idaho Company, Inc., P. O. Box 2800, Idaho Falls, Idaho 83401

A two-channel Bascom-Turner digital recorder is used to improve the flexibility of a DuPont thermal analysis system. The recorder inputs are connected directly to the outputs of a DuPont Model 990 Programmer/Recorder to permit data acquisition, storage, and reduction during TGA, DSC, and high temperature DTA runs on the DuPont system. Data, which is acquired at a fixed sampling rate, is stored on a floppy disk for further processing and reduction by the digital recorder. Its use for manipulation of the data, such as normalizing, rescaling, or offsetting, will be demonstrated. The results from various thermal analysis experiments on a sample are recalled, scaled, and plotted versus temperature on the same graph for ease of comparison. Use of the digital recorder system minimizes the need for repeating thermal analyses because the data is not lost even if the DuPont analog recorder runs off scale. It greatly increases the flexibility of the DuPont 990 Programmer/Recorder and thermal analysis modules. To permit more complex and extensive processing of data, the system is used with an HP-85 Personal Computer

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195 THE USE OF A DRY CAPILLARY INJECTION SYSTEM IN TRACE LEVEL ANALYSIS OF DIETHYLSTILBESTROL BY CAPILLARY GC/MS. William J. Morris, and Gene J. Nandrea, U.S. Food and Drug Administration, Denver, Colorado.

Using packed columns and EC detectors in the analysis of perfluorinated derivatives of diethylstilbestrol (DES), an ultimate sensitivity of 1-10 picograms is achieved. However, when dealing with complex sample matrices such as tissue, urine and feces, serious interferences are experienced. These interferences are often severe enough to preclude positive identification and accurate quantitation. This is particularly true in the case of the cis isomer of DES. The use of capillary GC/MS has provided the solution to this problem and allows us to identify both the cis and trans isomers. However, the use of a standard capillary injector restricts total volume to 2-2 lambda. Concentration of trace level extract solutions, frequently, caused solidification or formation of a gel. The use of the dry capillary injector permits large injection volumes up to 500 lambda and thereby overcomes previous injection restrictions.

196 THE USE OF A SEQUENTIAL INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETER FOR THE QUALITY CONTROL OF LEAD SMELTER OPERATIONS
F.J. Szydlowski, J. Massa and G. D. Haines

A sequential ICP spectrometer was used to determine Fe, Si, Ca, Mg, Zn, Pb, Al, Cu, and S in lead blast furnace slag and sinter samples. This data was then used for the quality control of blast furnace and sinter plant operation. Samples were taken into solution using a HCl:HF:HNO_3 pressure digest (USBM RI8480) for silicon and metals and a KBr/$KBrO_3$ oxidation for sulfur. All solutions were then taken up in 20% HCl. A corrosion - resistant torch assembly was used throughout this study. Sulfur was analyzed at the 182.04 nm line under nitrogen purge. All elements were background corrected.

197 SOIL AND PLANT CONCENTRATIONS OF CADMIUM AND ZINC IN THE VICINITY OF A SMELTER
M.E. Farago* and J.T. O'Connell, Chemistry Department, Royal Holloway and Bedford Colleges, Egham Hill, Surrey TW20 OEX, UK. (*Visiting Fellow, 1982-83, Cooperative Institute for Research in Environmental Sciences, Univ. of Colorado, Boulder, CO USA)

Cadmium, zinc and lead concentrations in soils and plants near a smelter at Avonmouth are reported for samples collected in May 1979 and in May 1980. The total metal soil concentration fall as distance from the smelter increases and decreases rapidly with depth for cadmium and zinc. The concentrations of these two metals are highly correlated at all depths. Near the smelter, where the carbon content and pH values of the soils are lowest, almost all the cadmium, as measured by EDTA extraction, is available. Concentrations of metals in plants also decrease with distance from the smelter, with concentrations being lower in samples collected in 1980. This is probably due to a seasonal variation in biomass, producing a dilution effect. We conclude that uptake of cadmium and that of zinc by grass species have different relationships to the carbon content of the soil.

198 PLATINUM METALS AND PLANTS: LOCATION OF PLATINUM METALS IN PLANT TISSUES
M.E. Farago* and P.J. Parsons, Chemistry Department, Royal Holloway and Bedford Colleges, Egham Hill, Surrey TW20 OEX, UK, (*Visiting Fellow, 1982-83, Cooperative Institute for Research in Environmental Sciences, Univ. of Colorado, Boulder, CO USA.)

The biological effects of platinum group metals on water hyacinths (Eichhornia crassipes MART. Solms) were investigated using hydroponic techniques. Relative toxicities were: Pt^{2+} $Pd^{2+} > Os^{4+}$ $Ru^{3+} > Ir^{3+}$ $Pt^{4+} >> Rh^{3+}$

The metals were deposited mostly in the roots. Toxic symptoms of Pt^{2+} complexes included the appearance of reddish-brown streaks in the leaves, whilst Rh^{3+} appeared to exhibit a a tonic effect. Root and leaf samples of Eichhornia crasspies containing the platinum metals were examined by a number of techniques, including scanning electron microscopy with energy dispersive X-ray analysis (SEM + EDXA). Control root and leaf specimens showed high concentration of Ca and smaller amounts of P and S. Roots treated with $[PtCl_6]^{2-}$ were covered in electron dense deposits. EDXA showed Ca (K_α, 3.96keV) and Pt(M_α, 2.05keV; L_α, 9.44keV; L_β, 11.07keV). X-ray photo-electron spectra of these deposits showed a corrected Pt 4f binding energy of 76±0.5eV, indicating Pt^{4+} in the deposits.

Electron microprobe analysis (EMPA) examination of Pt-treated roots showed clearly that platinum accumulated in the epidermal region, lesser amounts are in the cortex. Ruthenium, however, was distributed more evenly.

199 DEVELOPMENT OF A NEW FT-IR SPECTROMETER
Joel P. Covey, David R. Mattson, Mattson Instruments, 6333 Odana Road, Madison, WI 53719

An optical design of a new Fourier transform infrared spectrometer will be described. The bench-top spectrometer has a resolution of .12 cm^{-1}, can cover the NMR, MIR and FIR spectral regions with interchangeable beamsplitter and detectors and has several unique features.

The interfermeter is equipped with corner cube retro-reflectors for ultra-high stability. It's servo system uses laser quadrature detectors to control the direction and velocity of the moving mirror allowing the spectrometer to collect spectra in both directions. Because of this and the extremely high duty cycles over twenty spectra per second can be collected.

A second unique feature is the user reconfigurable sample compartment. Unlike conventional spectrometers where the entrance and exit optics are fixed, the user can change the F numbers, focal length and infrared spot size to match his sample. Moreover, the focusing optics can be removed completely and replaced with throughput matched high efficiency sampling accessories. Changeover from one configuration to another takes only a few minutes and because of the mechanical design of the components, no optical alignment is necessary.

200 HIGH SPEED MICROCOMPUTERS FOR FOURIER TRANSFORM INSTRUMENTS
P.J. Coffey, D.R. Mattson, Mattson Instruments, 6333 Odana Road, Madison, WI 53719

Super-micro computer technology has evolved to the point where powerful systems are now available for the analytical laboratory. The power, speed, and software available for these modern computer systems promise to revolutionize utilization and processing of spectral data.

This paper will discuss the use of a Motorola 68000, 32 bit super-micro system for significantly improving infrared and NMR data processing. The STARLAB computer system used for this application operates under the industry standard UNIX operating system. UNIX gives the STARLAB data base management, communication to other computers, and true multi-user/multi tasking operation. The STARLAB system employs a second 16-bit microprocessor solely for communications, data acquisition, and interrupt service. This reduces the I/O overhead requirements for the central 32 bit super-microprocessor and the UNIX operating system. The result is a very fast, efficient system that can handle communications and data transforms while maintaining good response time for several users.

The system provides communications to and from most computerized infrared and NMR spectrometers. The super-micro has sufficient speed to perform real time Fourier transforms and associated data reduction appropriate for FT-IR and FT-NMR applications.

The computer system can be used to significantly enhance the utilization of an NMR/IR laboratory facility. The STARLAB computer can be networked to the spectrometers in a "star" fashion, with each spectrometer communicating with the UNIX system in the center of the star. This configuration will allow each of the spectrometers to transmit data to a central system for storage, (up to 160 M bytes on-line) retrieval and data reduction. If data reduction is performed by the computer at the center of the star (which is a true multi-user system) then the spectrometers may be more efficiently utilized for the acquisition of spectra.

In many cases, the addition of one of these central super-micro systems will:

* provide greater spectral measurement efficiency than the addition of several spectrometers.
* cost less than the addition of a corresponding amount of disk memory to an older generation mini computer/spectrometer.

The use of a complete modern system at the center of the laboratory star network makes available all modern computer peripherals to each of the older generation computerized spectrometers. Peripherals such as letter quality printers, floppy disks, streaming tape, communications, Ethernet, graphics terminals, etc., are generally supported (hardware and software) on the central system. The communications facilities of the STARLAB system even can enable the user to operate spectrometers and process data from a remote site via modem/phone line connectors. STARLAB supports display graphics, plotter graphics and printing for a remote work station for under $5000 including 1200 baud phone connection.

This paper will discuss the architecture of this modern laboratory computer system. Also the capabilities in terms of data processing, speed, number of users, data storage, etc. will be presented.

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201 A NOVEL PROCEDURE FOR IMPLEMENTING THE MOLE-RATIO METHOD. P. MacCarthy, A. Vella and Z.D. Hill, Dept. of Chemistry/Geochemistry, Colorado School of Mines, Golden, CO 80401.

The mole-ratio method is commonly used in analytical chemistry for determining the composition and stability constants of complexes. This procedure is conventionally carried out in a batch-wise mode where a series of solutions are prepared all of which have a fixed analytical concentration of one reagent, say metal, and varying concentrations of the ligand. This paper describes a titrimetric procedure for acquiring identical data. We refer to the new procedure as a "contamination titration" in that the titrant is "contaminated" with the titrand at an identical concentration as that in the analyte solution. As an example, when 0.1F Cu^{2+} is titrated with a mixture of 0.1F Cu^{2+} + 0.3F $EDTA^{n-}$, the analytical concentration of metal ion in the titration flask remains constant (at 0.1F) while the analytical concentration of ligand gradually increases, thereby satisfying the requirements of a mole-ratio method. Advantages of the new procedure are discussed, and it is explained how this method conveniently circumvents cumbersome procedures adopted by some workers in related experiments.

202 **LASER SPECTROSCOPY AND PHOTOPHYSICS OF SYNTHETIC PHOTOREACTION CENTERS**
J. S. Connolly,‡ J. R. Bolton,* A. Siemiarczuk,* T.-F. Ho,* and A. C. Weedon,*
‡Photoconversion Research Branch, Solar Energy Research Institute, Golden, Colorado, 80401, and *Department of Chemistry, The University of Western Ontario, London, Ontario, N6A 5B7.

We are using laser flash photolysis and nanosecond lifetime fluorometry to study light-induced intramolecular electron transfer in covalently linked porphyrin-quinones. These molecules (PQ) consist of a tetratolylporphyrin linked to p-benzoquinone by a diamide bridge separated by 2-4 methylene groups. Shorter fluorescence lifetimes and reduced quantum yields in PQ relative to the unlinked porphyrin are interpreted as being due to intramolecular electron transfer from the lowest excited singlet state of the porphyrin to the quinone. Electron transfer appears to be thermally activated at temperatures above ~200K with an activation energy of 6-9 kJ/mole; at 295K the rate constant is ~2 x 10^8 s^{-1}.

Laser flash photolysis of these PQ systems induces absorption changes due to the porphyrin triplet state as well as a shorter-lived species whose optical spectrum is assigned to the charge-separated state P^+Q^-. The lifetime of this species is ~500 ns at 295K and ~50 μs at 110K. These data also indicate that the primary route of electron transfer in PQ is via the excited singlet and not the triplet state of the porphyrin. These relatively simple PQ systems appear to constitute a rudimentary model of the reaction centers of biological photosynthesis.

203 PARAMETERS EFFECTING MAGNETIC FIELD FLOW FRACTIONATION OF METAL OXIDE PARTICLES. T. C. Schunk, J. Gorse, M. F. Burke, Department of Chemistry, Unviersity of Arizona, Tucson, AZ 85721.

In recent years the technique of field flow fractionation (FFF) has been shown to be important in separations of particles in the micrometer size range. Separations of many materials have been demonstrated by the use of various fields which take advantage of different physicochemical properties of the particles. In this paper a new FFF technique will be discussed which employs a magnetic field for the study of metal oxide particles. Since retention in magnetic FFF is a function of a number of variables a great deal of information may be gained about both the physical and chemical properties of the sample material. In addition to the usual parameters influencing a FFF experiment (e.g., channel dimensions, flow profile, applied field, etc.) other factors specific to magnetic FFF need to be considered. The magnetic susceptibility of both the particles and the solvent, as well as the particle volume and field intensity determine the magnetic induced force. This in turn impacts on particle retention. Information on particle size, shape, magnetic susceptibility, etc., may thus be obtained from average particle retention. Peak shape also provides information on the distribution of these properties in the sample material.

204 THE STUDY OF SMALL PARTICLE DISPERSIONS WITH MAGNETIC FIELD-FLOW FRACTIONATION. J. Gorse, T. C. Schunk, M. E. Purnell, Department of Chemistry, University of Arizona, Tucson, Arizona 85721.

Field-flow fractionation is a separation technique for small particles in the size range of 0.01 to 10 micrometers. Field-flow fractionation has been called "one phase chromatography," since it is an elution technique involving liquid dispersions of small particles which are carried through an open channel by a flowing stream. Selectivity is developed by applying a force field at right angles to the flowing stream. The use of a magnetic field has been proposed, but not demonstrated until recently in our laboratory. In order to separate small magnetic particles, their dispersion in the liquid carrier must be stable during the time frame of the experiment. Floccullation of the particles is due to the interplay of coulombic, dispersive and magnetic forces. Since the application of a magnetic field to small particles increases the rate of floccullation by inducing attractive forces between particles, the dispersion stability of magnetic particles is of particular importance for magnetic field-flow fractionation. Experiments have shown a strong dependence of detector response on particle concentration, carrier composition, carrier flow rate, concentration of dispersing agents, and magnetic field strength upon dispersions of iron oxide particles. These changes manifest themselves in terms of changes in peak height, peak shape and retention times. Data to this effect will be presented and discussed.

205 A NEW NITROGEN ANALYZER FOR RAPID AND ACCURATE NITROGEN DETERMINATION. T. M. Jackson Erba Instruments Inc., 4 Doulton Place, Peabody, MA 01960

A new automatic Nitrogen Analyzer Model 1500 will be presented for the analysis of nitrogen in the range of 100 ppm to 100%.

The operating principal is a modification of the Dumas method and consists of weighing the solid or liquid sample into a tin container which is then sealed and loaded into a 50-seat automatic sampler.

The sample drops into an oxidation furnace which is maintained at 1000° and has a constant stream of helium carrier gas flowing through it.

As the tin container and sample drop into the furnace, it meets a plug of oxygen and due to the presence of tin and oxygen a strong exothermic reaction takes place, - flash combustion - at a temperature of approximately 1800°. This means that the analyzer is suitable for a wide range of inorganic, organic and organo-metallic compounds.

After flash combustion, the mixture of gases pass over an oxidation catalyst and from there through a second furnace which contains a reduction tube packed with copper and quartz chips. In the reduction tube, the surplus of oxygen is removed and any oxides of nitrogen which have been formed are reduced to elemental nitrogen. The mixture of gases, carbon dioxide, water, and nitrogen then pass through two filters which remove the carbon dioxide and water leaving the nitrogen to pass through a chromatographic column and then a thermal conductivity detector.

By simply removing the carbon dioxide trap, the analyzer may be used as a carbon analyzer or a CN analyzer. The data processing will allow calculations of percentage nitrogen, percentage carbon and C/N ratio.

Typical applications include agriculture, foodstuffs, milk, textiles, explosives, metallogy, oils, and clinical chemistry.

206 INNOVATIVE WET-AIR OXIDATION TREATMENT OF SELECTED WASTEWATERS BY THE VERTICAL TUBE REACTOR. Christina B. Cassetti and Bruce K. Kent, Applied Science & Engineering, Incorporated, 3244 South Platte River Drive, Englewood, Colorado 80110.

The Vertical Tube Reactor (VTR) was designed to oxidize organic wastes, too strong or toxic for biological units, using the principles of wet oxidation. The VTR consists of concentric tubes, making up a waste flow system and a heat exchange system, suspended in a deep well. As the waste travels down it attains the high pressures and temperatures required to initiate the combustion reaction. The heat generated during an exothermic reaction can be removed by the heat exchange system as a potential energy source. The reacted waste returns to the surface for disposal or further treatment as required. A bench scale laboratory reactor (LBR) was constructed to demonstrate VTR capabilities. A sample placed in the LBR is subjected to the temperatures and for the reaction times expected in the VTR. Correlation studies between LBR and a pilot scale reactor support using LBR treatability data to model expected reduction rates in a full scale VTR. Presented here are treatability data generated from three synfuel wastewaters and a municipal sludge processed with the LBR.

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207 A DIRECT CALCULATIONAL TECHNIQUE FOR MAKING CORRECTIONS FOR CORRIGIBLE SYSTEMATIC ERROR IN ANALYTICAL RESULTS. Mario J. Cardone and Jay G. Lehman. Norwich Eaton Pharmaceuticals, Inc., Norwich, New York 13815.

The techniques for correcting real sample analysis results to get the correct value provided that no incorrigible errors are present have been described elsewhere and the properties of the data set as previously described are employed. This data set utilizes only five or six real sample analysis values over the linear dynamic range of interest (Youden Regression Curve) and two or three data points to describe the Method of Standard Additions (MOSA) curve. In the calculation, extrapolation to an infinite size sample is made. A regression line from the data set is obtained for the relationship between the concentration values and the reciprocal sample weights. The intercept of this regression line provides the corrected analysis result. If the ordinate concentration values of the regression line are calculated from the raw data using the slope of the reference standards curve, the intercept value has been corrected for the constant error (C.E.) bias. If, however, the slope of the MOSA curve is used, the intercept value has been corrected for both the C.E. and P.E. (proportional error) bias. In quality assurance applications where only the correct value is the issue, this direct calculational technique promises to be of particular interest. The usual diagnostic interpretations, however, can still be made.

208 An Electronic Transducer for the Automated Determination of Integrated Gas Volumes. Catherine Hyndman, Morris Bader, Ph. D., Department of Chemistry, Moravian College Bethlehem, PA 18018

The automated measurement of gas volumes has always posed a severe problem in the study of chemical reactions. To our knowledge, the apparatus to be described may be the first of its type. The apparatus has been used most successfully to follow the kinetics of the enzymatic decomposition of H_2O_2 by accurate determination of the released oxygen gas. The purpose of that experiment was not only to study the kinetics of the enzyme catalase, but to determine the mechanism of its inhibition by various enzyme poisons, namely, cyanide, fluoride, azide, and the anti-cancer drug, 5-fluoro-uracil.

The basic concept of the apparatus is that we are able to measure the change in resistance of an aqueous conducting solution which is being displaced by the evolved gas. Through a series of electronic transducers, we are then able to produce a voltage directly proportional to the volume of the gas evolved. This output voltage can then be processed by any number of standard methods. A more detailed description of the apparatus will be presented.

209 USE OF STANDARD ADDITIONS IN NATURAL WATER SYSTEMS, W.C. Gorman, Jr. and R.K. Skogerboe, Department of Chemistry, Colorado State University, Fort Collins, CO 80523. P.W. Davies, Colorado Division of Wildlife, 313 West Prospect, Fort Collins, CO 80522.

Typically, metal concentrations in natural waters are determined through the use of standard additions. Natural waters are known to complex various heavy metals but this complexation is a very slow process, taking several hours to a few days.

If the standard addition is added just prior to analysis, there is not adequate time for metal-complex equilibrium to be reached, causing the original metal concentration to be underestimated.

In this paper, a comparison will be made between freshly added standard additions and standard additions which have been aged for several days, through the use of DPASV. This will be followed by a discussion of which method of standard additions gives the best estimate of the true free metal concentration.

210 ION EXCHANGE STUDIES OF METAL-MULTILIGAND EQUILIBRIA. T.F. Rees, S.R. Daniel, G.C. Smith and P. MacCarthy, Dept. of Chemistry/Geochemistry, Colorado School of Mines, Golden, CO 80401.

The geochemical behavior of metals often involves systems where the metal is complexed by different ligands simultaneously. A theoretical model describing such systems has been published (MacCarthy, 1977; MacCarthy and Smith, 1979). This model predicts that for systems of large total ligand/metal ratios, the binding of the metal to the multiligand mixture is characterized by a constant which is a weighted average of the conditional stability constants of the individual complexes in the system. This paper reports experimental validation of the model using stability constants determined by the Schubert ion exchange technique and comparing the calculated result to experimentally determined values using two-ligand and three-ligand mixtures. The results indicate that the algorithm accurately predicts the complexation behavior of neptunium(V) in simple multiligand systems where only 1-1 complexes are formed.

MacCarthy, P., J. Envir. Sci. Health, A12(1&2) 43-59(1977).
MacCarthy, P. and Smith, G.C. in "Chemical Modeling in Aqueous Systems", E.A. Jenne (Ed.), A.C.S. Symposium Series, No. 93(1979).

211 SINGLE COLUMN ION CHROMATOGRAPHY. J. E. Girard, Department of Chemistry, The American University, Washington, D.C. 20016

Single column ion chromatography (SCIC), which uses conventional high pressure liquid chromatography (HPLC) instrumentation and a conductivity detector, has been shown to be a low cost analytical technique for the determination of inorganic anions. New types of ion exchange columns have expanded the application of this method. By carefully choosing the column, eluting species, its concentration and the pH, improved sensitivity, chromatographic efficiency, selectivity and resolution may be achieved.

When the single column ion chromatograph is coupled to a ultraviolet (UV) or electrochemical (either amperometric or coulometric) detector, it becomes an efficient method for separating and quantitating metal cations.

The application of single column ion chromatography techniques to industrial water analysis will be presented.

212 A SEQUENTIAL METHOD OF ANALYSIS FOR FLUORIDE AND CHLORIDE BY ION CHROMATOGRAPHY, Juan J. Rios and Vincent C. Anselmo, Texas Air Control Board, 6330 Highway 290 East, Austin, Texas 78723.

There are generally two options available if a laboratory wants to analyze for fluoride or chloride by ion chromatography in a given matrix. Either the sample is processed to remove interfering species or the sample is analyzed for all the anionic species present. There are other analytical methods, such as specific ion electrodes, which can be used to analyze a sample directly, but this paper will concentrate solely on ion chromatography. A procedure is described in which a solution is analyzed for fluoride or chloride only in the presence of other ions. A dilute eluent is used so that only the species in question is rapidly eluted while the other anions are retained on the column. Following a certain number of analyses the other anions break through the column. At this time the column is washed with a higher concentration of eluent and then allowed to come to equilibrium with the original eluent. Under these conditions, and using a chemically supressed system, seven samples containing fluoride will be eluted before chloride begins to interfere. The eluent used was 0.5 mM $NaHCO_3$. Similarly, five chloride samples were eluted, using 1.5 mM $NaHCO_3$, before phosphate interfered. In each case the column was regenerated by eluting with 9.6 mM Na_2CO_3 and 12 mM $NaHCO_3$ for 5 minutes followed by re-equilibration with the original eluent, which for fluoride took 60 minutes and 15 minutes for chloride. Data representing accuracy, precision, and reproducibility will be presented.

213 ION CHROMATOGRAPHIC ANALYSIS OF INDOOR AND OUTDOOR AEROSOL PARTICLES COLLECTED ON TEFLON FILTERS. S.R. Kelty, L.A. Psota-Kelty, J.D. Sinclair, and C.J. Weschler. Bell Laboratories, Holmdel, New Jersey 07733

Rocky Mountain Conference, Magnetic Resonance, Vol. 15, [illegible] Art.

Indoor and outdoor dusts were collected on Teflon membrane filters using dichotomous air samplers that were placed on the roof and in the equipment room of telephone switching centers. Locations studied to date are Lubbock, Texas and Wichita, Kansas. The filters were changed twice as often outdoors as indoors to compensate for the larger concentration of outdoor dust.

The dust-loaded filters were each extracted in 10 mL of distilled-deionized water. An ultrasonic bath was used for approximately one hour to aid in the extraction. The extracts were analyzed for chloride, nitrate, sulfate, sodium, ammonium, potassium, calcium, and magnesium using ion chromatography. The major ionic constituents in the coarse (2.5-15 μm dia.) and fine (< 2.5 μm dia.) aerosol particles, both indoors and outdoors, have been identified. Comparisons of indoor and outdoor ion concentrations in the coarse and fine dust fractions have provided information on the sources of the ionic species in indoor dust.

214 ACCUMULATION RATES OF IONIC SUBSTANCES ON INDOOR SURFACES. G.B. Munier, L.A. Psota-Kelty, and J.D. Sinclair. Bell Laboratories, Holmdel, New Jersey 07733.

The accumulation rates of water soluble ionic species that collect on horizontal and vertical indoor surfaces have been determined for sites in more than 15 cities in the United States. Zinc and aluminum surfaces exposed for 8-15 years to electronic equipment environments have been sampled by a filter paper extraction technique. Chloride, sulfate, nitrate, bromide, sodium, ammonium, potassium, calcium, and magnesium concentrations were determined by ion chromatography. The ranges of accumulation rates of chloride and sulfate determined to date are approximately 0.05-0.7 μg chloride/cm^2/yr on zinc, 0.02-0.4 μg chloride/cm^2/yr on aluminum, 0.1-1.3 μg sulfate/cm^2/yr on zinc and 0.1-0.9 μg sulfate/cm^2/yr on aluminum. Comparisons between indoor accumulation rates and tropospheric concentrations or dry and wet deposition data have been undertaken. Comparison of horizontal and vertical accumulation rates provides insight, in some cases, about the origin of the substances.

215 NEW DEVELOPMENTS IN ION CHROMATOGRAPHY. Christopher A. Pohl, M.E. Ebenhahn, S. Papanu, G. Hennion and A. Woodruff, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94086

Three new developments of ion chromatography have been completed. New high performance anion materials, new eluent systems for MPIC, and cation exchange materials produced with newly developed cation latexes.

Two new micropellicular anion exchange materials have been introduced. The first is used in the AS6 column for the analysis of carbohydrates and the second is used in the AS7 column and is used in the analysis of polyvalent ions. Typical efficiencies for these columns are 20,000 to 40,000 plates per meter.

A new eluent system has been developed for MPIC. It allows the use of MPIC in the analysis of chelating agents. The system can also be used in the analysis of complexed metals.

Columns produced with cation latex have been developed. They exhibit superior selectivity to the older surface sulfonated materials.

ANION SEPARATIONS BY ION CHROMATOGRAPHY USING DILUTE ELUENTS
Ralph E. Truitt, Celanese Research Company, 86 Morris Avenue, Summit, N.J. 07901

216 Ion chromatography (IC) is particularly useful for the separation of anion mixtures because it is rapid and specific. The use of conductance detection often allows anion determinations below the limits of photometric detectors that are commonly used in ion exchange chromatography. However, separation of some carboxylic acid anions is still difficult by double column IC, principally due to the limited choice of mobile phases. The purpose of this study was to measure anion retentions and resolutions using dilute mobile phases with double column IC. A mixture of carboxylic acids, a mixture of inorganic salts and a mixture of strong organic acids were analyzed using five eluents. The study showed that, in general, dilute mobile phases greatly increase analysis time with little improvement in separations. One outstanding exception was dilute KOH, which provided improved resolution of C_1-C_6 carboxylates.

217 A 12-MINUTE ISOCRATIC SEPARATION OF SULFITE, SULFATE, AND THIOSULFATE BY SINGLE-COLUMN ION CHROMATOGRAPHY (SCIC). **Thomas H. Jupille**, David W. Tosami, and David E. Burge, Wescan Instruments, Inc., 3018 Scott Blvd., Santa Clara, CA 95050

The simultaneous analysis of sulfoxy anions is of interest in areas as diverse as pulp/paper processing and photography. Until recently, ion chromatographic separation of these species has meant either a long analysis time or the need for two separate isocratic runs. Recent work (1) has described a gradient system which reduces the single-run analysis time to less than 20 minutes.

This paper describes the use of a short (10 cm) column with a phthalate eluant for the isocratic separation of sulfite (as bisulfite), sulfate, and thiosulfate in 12 minutes. The system requires no column reequilibration and no suppressor regeneration between runs.

218 RECYCLE ION CHROMATOGRAPHY FOR TRACE IONS IN DRINKING WATER.
T. B. Hoover and G. D. Yager, Environmental Protection Agency, Athens, Georgia 30613.

Trace anions were separated from interfering major components by collecting appropriate portions of the chromatographic peaks, after suppression, on concentrator columns for reinjection. The utility and limitations of the technique will be discussed with reference to the determination of arsenate, selenite, and selenate in drinking water and water supplies, where nitrate and sulfate may be in several-hundred-fold molar excess.

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219 COMPARISON OF ION CHROMATOGRAPHY TO ION ANALYSIS METHODS NOT EMPLOYING ELUENT MODIFICATION. John Stillian, Chris Pohl and Ed Johnson, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94086

A wide variety of techniques have been developed in the past eight years for the chromatographic analysis of ions. While some work has been done to compare these new techniques, no general comparison of suppressed and non-suppressed techniques has been made.

While it is well known that the suppressor imparts high sensitivity to the ion chromatography system, several less obvious benefits are obtained through the use of chemical suppression. A major benefit of chemical suppression is the increased linear range of such an analysis system. Single column analysis systems provide considerably smaller linear ranges than a corresponding suppressed system.

Another benefit of suppression is a decreased sensitivity to environmental factors. Non-suppressed systems invariably exhibit high sensitivity to flow and temperature variations.

Suppressed systems also provide a major benefit in terms of sensitivity to interferences. Single column systems are prone to interferences from eluent components, analyte counterions, and in some cases from non-ionic components. All of these factors severely limit the usefulness of non-suppressed techniques to "real" samples.

220 OXIDATIVE PYROLYSIS/ION CHROMATOGRAPHY - A NOVEL APPROACH TO ORGANIC ELEMENTAL ANALYSIS. Dutt V. Vinjamoori, Corporate R&D Staff, S4A, Monsanto CO, 800 N. Lindbergh Blvd., St. Louis, MO 63167

Trace determinations of 'S' and 'Cl' in organic liquids, solids and gases have been two of the most important and challenging problems in the elemental analysis of a wide variety of industrial chemicals. We will present two novel sample decomposition techniques, which involve the use of controlled combustion for organic liquids using a constant rate injector and programmed temperature pyrolysis for solid samples. These techniques add new dimensions in the sample preparation step for subsequent determination of S and Cl as SO_4^{-2} and Cl^- by Ion Chromatography. Unlike the oxygen flask or oxygen bomb techniques, these approaches not only allow the control of combustion rate but also permit the use of large sample volumes or sizes, because of temperature programming and incremental introduction of the sample into the pyrolysis zone. Experimental techniques for the collection of combustion products using solid sorbents and optimum sample decomposition procedures will be presented. Applications to the determination of S and Cl in a variety of complex organic matrices including the extension of this work to organo F, Br and I will also be discussed.

221 ION CHROMATOGRAPHIC DETERMINATION OF VALPROIC ACID.

H. Itoh and Y. Shinbori, Faculty of Pharmaceutical Sciences, Josai University, Sakado, Saitama, 350-02, Japan.

Valproic acid(di-n-propylacetic acid) is the free acid form of the drug marketed under the names of Epilim, Sodium Valproate, and Depakine, which have been used as an anti-epileptic drug. Since the acid is non-chromophoric species and has a tendency to absorb on the column, the usual " High performance liquid chromatography " is not effective.

At the 24th Rockey Mountain Conference, we reported the ion exclusion technique using a carbonic acid solution as an eluent and the application to the analysis of acetate in some pharmceutical samples. Now, we describe a new method for the determination of valproic acid in drug and human plasma as an example of the application of this technique. This method is simple and non-expensive compared with gas-liquid chromatography and enzyme immunoassay being used for the estimation of valproic acid in plasma. Analytical data and plasma levels of the acid will be presented.

222 EVERYTHING YOU EVER WANTED TO KNOW ABOUT BORIC ACID ANALYSIS BY IC. Denise Eubanks, Lani Angers, and A.W. Fitchett, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94086

There are three different levels of boric acid analysis where Ion Chromatography has been applied: This first is high level determination of boric acid, such as typical in the nuclear power industry where levels from 100 ppm to 4000 ppm are not uncommon. The second is trace level determination of boric acid such as in environmental waste streams or again in the nuclear power industry. Here levels less than 10 ppm are usually desired. The last area is the anlaysis of pure boric acid for impurities such as chloride, nitrate and sulfate which can act as corrodants in certain systems. Again the nuclear power industry is a prime example. This paper will deal with all aspects of boric acid analysis as it pertains to these three different level requirements.

223 DETERMINATION OF LOW CONCENTRATIONS OF MONOSACCHARIDES, AND ALCOHOLS BY ION CHROMATOGRAPHY WITH PULSED AMPEROMETRIC DETECTION. Roy D. Rocklin, Christopher A. Pohl and Edward L. Johnson, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA. 94086

Most saccharides have pKa values between 12 and 14, thus allowing their separation as anions by ion exchange chromatography using sodium hydroxide eluents. This separation mode, when combined with the detection mode of pulsed amperometry, provides a selective and highly sensitive method for determining low (sub PPM) concentrations of sugars. Retention time can be controlled during anion exchange chromatography by the addition of a pusher ion such as acetate. The addition of 0.2 M sodium acetate to the 0.15 M sodium hydroxide eluent elutes oligosaccharides such as DP2 through DP10 in 10 minutes.

The detection mode is pulsed amperometry. The detection limits using pulsed amperometric detection are 30 ppb for sugar alcohols and 100 to 300 ppb for monosaccharides and oligosaccharides. These detection limits are 10 to 100 times lower than those obtained using a refractive index detector, the most common method.

Alcohols can be separated on a high capacity cation exchange column using 0.1 N $HClO_4$ eluent and detected by pulsed amperometry. This method is particularly useful for determining alcohols of low volatility such as glycerol.

224 ANION ANALYSIS BY CONVENTIONAL HPLC. Joan D. Newburger and W. Roy Day, Waters Associates, Inc., 34 Maple Street, Milford, MA 01757.

Traditional Ion Chromatographs™ required a special suppressor column in series between the separator column and a conductivity detector. Through new column technology, it is now possible to eliminate the suppressor column and treat ion chromatography as one more area of conventional HPLC. A study has been undertaken to compare commercially available high capacity and low capacity anion exchange columns. Just as with reversed-phase chromatography, selectivity can be achieved by varying buffer concentration and pH. Optimization of anion separations and the benefits and limitations of such columns will be discussed. Detection methods suitable for ion analyses have also been examined. These include refractive index and UV detection (absorbance and vacancy methods) as well as conductivity detection. An analysis of factors influencing the choice of a particular detector for specific columns and uses will be presented.

225 AUTOMATED ION CHROMATOGRAPHY. S. H. Hoke and L. J. Baxter, US Army Medical Bioengineering Research and Development Laboratory, Ft Detrick, MD 21701

A Dionex Model 16 ion chromatograph has been automated by means of a Gilson automatic sampler supplied by Dionex, a Varian Vista 401 data processor, and an Apple II computer. Since the Model 16 ion chromatograph does not readily lend itself to automation, some modifications had to be made. The automatic sampler, sampler pump and injection valve are all controlled by the Vista 401 which also identifies and integrates the data generated by the ion chromatograph. This information is then transmitted to the Apple II computer where it is quantitated from a linear fit of the calibration data and stored permanently on floppy disk for future retrieval. The automatic sampler holds sample vials up to 25 mL in volume. Thus, by substituting a concentrator column for the 0.1 mL sample loop, one can determine ppb levels of ions. The automatic sampler holds over 100 vials and therefore can operate unattended for several hours. By storing the data on floppy disk, it can be readily accessed, manipulated, and printed out in any form desired. By applying this degree of automation to ion chromatography we have greatly simplified analyses, and are able to employ some novel anion stripping techniques that otherwise could not be applied.

226 AUTOMATED ION CHROMATOGRAPHIC DETERMINATION OF ANIONS IN PRECIPITATION SAMPLES. G.S. Pyen, M. R. Brown and D. E. Erdmann. U.S. Geological Survey, National Water Quality Laboratory,6481-H Peachtree Industrial Boulevard, Doraville, Georgia 30340

A Dionex 2120 Ion Chromatograph[1/] has been modified for use with low level precipitation samples. Modifications include the installation of two pulseless pumps which permitted the automatic addition of a known amount of eluent to each sample. This eliminated the water dip, which interferes with fluoride and chloride determinations at low concentrations. Additionally by utilizing the Auto OffSet mode, it is possible to vary the output range for each anion according to it's 'expected' concentration range. Thus, a wider range of anion concentrations in typical precipitation samples can be measured without further dilution. Approximately 10 minutes is required to analyze six anions in each sample.

The detection limits for flouride, chloride, phosphate, bromide, nitrate, and sulfate are 0.01 milligram per liter. Relative standard deviations of less than 10 percent were obtained for each of four U.S. Geological Survey Standard Reference water samples. Additionally, comparisons for some anions were made with automated instrumentation using colorimetric and turbidimetric methods (chloride, phosphate, nitrate, and sulfate). The ion chromatographic results showed good agreement with those generated using automated techniques.

[1/]The use of trade name is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey.

227 DETERMINATION OF POLYVALENT ANIONS BY ION CHROMATOGRAPHY. A. Woodruff, Chris Pohl D. Eubanks, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA. 94086

A newly available separator column (Dionex AS7 Separator Column) when coupled with a post column reaction allows the rapid determination of polyvalent anions.

Analysis of polyvalent anions has been limited to indirect determination due to problems in separation and detection. Polyphosphates for example are typically determined by a digestion followed by a total phosphate determination. It has been reported that a chromatographic separation [1](P_1-P_4) followed by digestion and subsequent phosphate determination is possible (30 minutes), but, is expensive and separation is poor.

The detection problems have since been eliminated by a post column reaction followed by detection at 330nm.

The problem associated with separation has been the potentially large valencies that these ions can have (some as large as 10 or 12), hence requiring a step change. One can eliminate this problem by inhibition of ionization via a low pH mobile phase combined with a highly selective stationary phase resulting in an isocratic, rapid technique for these analyses. A rapid (15 minutes) and efficient separation of such anions as polyphosphates, NTA, EDTA; and phosphonates can now be achieved.

This paper will discuss linearity, detection limits and several areas of important industrial applications.

1. N. Yoza, K. Ito, Y. Hirai, S. Ohashi, J. Chromatogr., 196 (180) 471-480

228 NOVEL APPLICATIONS OF ION CHROMATOGRAPHY IN NUCLEAR POWER GENERATION. Joseph J. Law et al. Carolina Power & Light Company, P.O. Box 1551, Raleigh, North Carolina 27602.

New methodology of ion chromatographic analysis used in water chemistry control for electric power generation has been continuously developed. Successful monitoring of trace impurities in system water has enabled the generation stations to achieve better plant performance with higher efficiency and reliability. Benefits of reducing deposition, equipment corrosion, and formation of radioactive byproducts in the nuclear reactor are derived from the advancement of Ion Chromatography (IC). IC is valued for the rapid determination of trace chloride in reactor coolant with high borate concentration in the post-accident samples. Mobile Phase IC monitoring of the degradation products of ion-exchange resins, such as sulfonate and quaternary ammonium ions, used in the makeup water system and condensate polishers provides essential information of fouling and intrusion of resin fines into a boiling water reactor. On-line ion chromatographic measurement in the secondary water system has been installed in three pressurized water reactor plants. Carbon dioxide in-leakage in a gas-cooled reactor can be monitored with 20 ppb detectable limit using IC Exclusion. Other applications include the detection of trace organic compounds in feedwater for maintaining acceptable reactor coolant purity and the determination of morpholine and cyclohexylamine in the secondary water.

229 PLATING BATH ANALYSIS BY ION CHROMATOGRAPHY. Karen K. Haak, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA. 94086

The solutions used to electroplate a wide variety of products are primarily composed of ionic species that are easily determined by Ion Chromatography. Control of major and minor constituents are of extreme importance to ensure the quality of plated product.

Ion Chromatography can be used to rapidly and reliably detect, identify, and quantify a wide variety of plating solution constituents. Some species of special interest include metal complexes ($Au(CN)_2^-$, $Au(CN)_4^-$, $Co(CN)_6^{3-}$, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, $Ni(EDTA)^{2-}$, $Cu(EDTA)^{2-}$); common anions (Cl^-, Br^-, NO_3^-, HPO_4^{2-}, PO_2^{3-}, SO_4^{2-}, BF_4^-); cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}); organic acids (citric, formic, succinic) as well as carbonate and borate; transition metals (Fe^{3+}, Fe^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Pb^{2+}); surfactants such as sodium lauryl sulfate and a variety of organics commonly employed as additives such as saccharin.

230 DETERMINATION OF IONIC SPECIES OF CLINICAL SIGNIFICANCE IN CEREBROSPINAL FLUID BY HIGH PERFORMANCE ION CHROMATOGRAPHY USING CONDUCTOMETRIC DETECTION. Mark S. Davis, LDC/Milton Roy, P.O. Box 10235, Riviera Beach, Florida, 33404

The determination of multiple inorganic ions(e.g. Na^+, K^+, Ca^{++}, Mg^{++}) as well as other ionic species present in cerebrospinal fluid is described using single-column ion chromatography with conductometric detection. Limits of detection for species of clinical importance are assessed. Techniques for sample preparation are also presented.

231 Abstract not available.

232 HIGH-SPEED CATION SEPARATIONS BY SINGLE-COLUMN ION CHROMATOGRAPHY (SCIC) **David W. Tosami**, Thomas H. Jupille, and David E. Burge, Wescan Instruments, Inc., 3018 Scott Blvd., Santa Clara, CA 95050

Single-Column Ion Chromatography (SCIC) for the analysis of dissolved ions is most frequently carried out by ion exchange separation directly coupled to electrical conductivity detection. The direct coupling of detector to column outlet minimizes post-column dead volume and allows small-diameter packing materials and low-volume columns to be used for maximum efficiency and minimum separation time.

Previous work has demonstrated the application of SCIC to the analysis of anions with separation times measured in seconds rather than minutes (1). This paper extends the concept of high-speed ion chromatography to sub-one minute cation analysis.

1. Jupille, T., Burge, D., and Tosami, D.; Chromatographia, **16**, 312 (1982)

233 DETERMINATION OF CARBOXYLATE ANIONS BY ION CHROMATOGRAPHY. George Hennion and Chris Pohl, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94086

At the present time HPICE is the method used for determination of carboxylic acids. This has been due to poor column selectivity for carboxylate anions with MPIC or HPIC. This paper investigates the determination of lower molecular weight carboxylate anions by HPIC.

Enhancement in the column selectivity for mono and dicarboxylic acids with recently developed column technology will be discussed and compared to the current AS1 through AS4 HPIC column series. Eluent systems designed for the solution of particular carboxylate determinations will be presented. The use of the AS5 column in regard to selectivity for polyvalent carboxylate anions using hydroxide eluents will also be discussed. Results from some new experimental columns will be presented.

234 IMPROVED FIBER SUPPRESSORS FOR EXPANDED IC CAPABILITIES R. Slingsby, C. Pohl Dionex Corporation, 1228 Titan Way, Sunnyvale, CA. 94086

The most common post-column reaction used in ion chromatograph is chemical suppression of the system background conductivity. By use of suppression via ion exchange, medium and high capacity separator columns and eluents allowing optimum selectivities can be used. The chromatographer is allowed great flexibility in designing separations and sensitivities are enhanced.

The Anion and Cation Fiber Suppressors are the state-of-the art suppressors. In addition to being continuously regenerated, they provide enhanced resolution and sensitivity for many analytes including weak acids and bases. Application that use the fiber suppressors continue to grow as they are now used in HPIC, MPIC and ICE modes of ion chromatography.

As performance and lifetime of the fiber suppressors can be maximized by judicious choice of reagents and operating parameters, design and function and proper use of these suppressors will be discussed. New applications made possible through use of the fiber suppressors will be included.

235 THE DETERMINATION OF NITROGEN IN SILICATE BASED NITRIDE GLASSES USING CATION CHROMATOGRAPHY,* R. M. Merrill, Sandia National Laboratories, Albuquerque, New Mexico 87185

Nitrogen is incorporated in silicate glasses by adding silicon nitride to increase chemical durability. The nitrogen content of these glasses has been determined as the ammonium ion following conversion in a molten sodium hydroxide bath. Ammonia is formed according to the general equation:

$$SiON_x + NaOH \rightarrow NH_3(g) + Na_2SiO_3$$

The glass samples were mixed with sodium hydroxide pellets in nickel boats and heated to ~ 800°C in a tube furnace under a stream of argon. The released ammonia was trapped in a 1% boric acid solution and analyzed using cation chromatography techniques. Since there are no standard reference glasses with certified nitrogen contents available, electronic-grade silicon nitride was used as a standard. Glass samples with nitrogen contents ranging from less than 1% by weight to slightly more than 4% by weight were analyzed with a typical precision of ± 0.1% absolute. The total analysis time was slightly more than one hour. The results of the ion chromatography analyses will be compared with results obtained using an inert gas fusion procedure.

*This work performed at Sandia National Laboratories supported by the U.S. Department of Energy under Contract Number DE-AC04-76DP00789.

236 HIGH PERFORMANCE LIQUID CHROMATOGRAPHIC ANALYSIS OF ANIONS AND CATIONS IN SOILS. Karin L. Fitzpatrick and W. T. Frankenberger, Jr., Dept. of Soil and Environmental Sciences, University of California, Riverside, CA 92521.

High performance liquid chromatography can be used as a rapid and highly accurate method for the simultaneous determination of inorganic ions in soil extracts. Ions were extracted from six various surface soils using the following reagents: H_2O, 10 mM LiCl, 10 mM KCl, 10 mM $Ca(C_2H_3O_2)_2$, and 0.15% $CaCl_2$. Aliquots of 500 µl or 100 µl were injected into the mobile phase and ions were separated by low capacity exchange-resins. The detection mode used was conductivity. Phthalic acid (4 mM adjusted to pH 4.5 with sodium borate) was the eluent used for the determination of the following anions within 12 minutes: Cl^-, Br^-, NO_2^--N, NO_3^--N, $SO_3^=$-S and $SO_4^=$-S. Using the precolumn alone, without its subsequent anion exchange-resin column, $SO_4^=$-S and NO_3^--N detection can be completed within four minutes. Nitric acid (10 mM) was used as the mobile phase for the monovalent cation analysis of Li^+, Na^+, NH_4^+ and K^+ within five minutes. Ethylenediammonium dinitrate (5 mM adjusted to pH 6.1 with nitric acid) was the eluent chosen for analysis of Ca^{++}, Mg^{++}, Sr^{++} and Ba^{++} with detection completed within eight minutes. The detection limit was 25 µg/ml using the 500 µl loop.

237 CHEMICAL ANALYSIS OF FLUID INCLUSIONS BY ION CHROMATOGRAPHY, J. M. Thompson, S. S. Howe, and W. E. Hall, U.S. Geological Survey, Menlo Park, CA 94025

Fluid inclusions in minerals give information about the temperature and salinity of the liquid at the time of mineral deposition provided the inclusions were trapped as the minerals grew. Freezing and heating stage microscopic studies of fluid inclusions yield information on the NaCl equivalent salinity and homogenization temperature of the fluid. The purpose of this study was to assess the use of ion chromatography as a means of chemically analyzing fluid inclusions and to use cation geothermometers to estimate the temperature of the fluid during mineral deposition. Nine mineral samples were studied, including quartz, sphalerite, rhodochrosite, pyrite, and chalcopyrite from the Creede Mine, CO., and quartz from the Climax Mine, CO. Each sample was cut to approximately $1cm^3$, cleaned by constant potential electrolysis at 100 VDC for 36 hours, dried overnight in a vacuum oven at 110° C, and loaded into previously cleaned stainless steel tubes; the tubes were then sealed, evacuated, and crushed. Typically $1\text{-}10 \times 10^{-6}$g of water was liberated from the inclusions and the salts leached with three 20mL aliquots of distilled water while immersed in an ultrasonic bath for 10 minutes. Fluoride, Cl, Br, NO_3, and SO_4 were separated using a Dionex AS3 anion column and Li, Na, NH_4 and K using a Dionex CS1 cation column. Because a HCO_3-CO_3 solution is the eluent, HCO_3 and CO_3 were not determined by this technique. Calcium and Mg were analyzed by atomic absorption spectrometry. Four samples had cation-anion balances within 20 percent; the remainder had poor charge balances. Two of these poorly balanced samples were sulfides that may have oxidized during the electrolysis (excess sulfate was recovered) and one was a carbonate. All samples from Creede have calculated Na-K-Ca temperatures between 250-320°C; calculated Na-K temperatures between 270-350°C; and calculated salinities from 12-37 percent. In comparison, fluid inclusion homogenization temperatures at Creede are between 180-250°C and NaCl equivalent salinities range from 4-12 percent.

238 THE DETERMINATION OF FLUOROACETIC ACID BY ION CHROMATOGRAPHY.
Richard E. Buechele, Forensic Science Research and Training Center, FBI Academy, Quantico, Virginia 22135

Fluoroacetic acid and its sodium salt (compound 1080) are used as rodenticides. The use of 1080 is presently restricted, however there has been recent interest in lifting some restrictions. The determination of 1080 has always been difficult using conventional analytical methods. Direct analysis for small organic acids by gas-liquid chromatography is generally unsuitable. Liquid chromatography with UV detection is also inappropriate due to the low absorbance of 1080. Most standard approaches to 1080 determination involves derivitization, followed by either GC or LC analysis. The derivitization process either renders the 1080 stable for gas chromatography; or it attaches a UV absorbing or fluorescing group to allow detection in liquid chromatography. Liquid chromatography has been used with conductivity detection for determination of several organic acids. This method can be used for fluoroacetic acid, and does not require lengthy derivitization procedures. It may prove to be the qualitative and quantitative method of choice for 1080 determination. The instrumentation and conditions necessary for 1080 determination will be described. Limits of detection, linearity, selectivity, and applications will be discussed.

239 Ion Chromatography of Transition Metals, J. Riviello, C. Pohl; Dionex Corporation, 1228 Titan Way, Sunnyvale, CA. 94086

The separation of transition metals in ion chromatography depends upon complex ion formation. Complexing agents present in the eluent radically alter the ion exchange behavior of metal ions allowing for rapid and effective separations. By using chelating anions such as citrate, oxalate and tartrate, metal ions can be separated by anion or cation exchange.

The effect of eluent concentration, pH and the counter-ion in the anion and cation exchange separation of metal ions will be presented. These separations are accomplished using HPIC columns which contain pellicular ion exchange resins. Stationary phase factors such as ion exchange capacity, degree of polymer crosslink and the type of quaternary amine functional group (anion exchange) will be discussed.

Metals ions have also been separated using MPIC. Separations using this type of reverse-phase ion pairing method have been accomplished in both the anion and cation modes. A comparison of HPIC and MPIC for the separation of transition metals will be made.

240 ANALYSIS OF BROMIDE IN FOOD PRODUCTS BY SINGLE-COLUMN ION CHROMATOGRAPHY (SCIC). **David W. Tosami**, Thomas H. Jupille, and David E. Burge, Wescan Instruments, Inc., 3018 Scott Blvd., Santa Clara, CA 95050

Single-Column Ion Chromatography (SCIC) is broadly defined as the analysis of dissolved ions by liquid chromatography using an appropriate detector coupled directly to the column outlet. Although the most common approach to SCIC couples ion-exchange separation with electrical conductivity detection, other column/detector combinations can be used to increase selectivity or sensitivity specific cases. The analysis of bromide in food products (either naturally occurring or as a by-product of fumigation) is an example.

Ion-exchange separation of bromide from other halide ions is straightforward, but organic acids in the sample can interfere with bromide detection. The use of an amperometric detector avoids interferences, and allows rapid, sensitive bromide determination.

241 "THE CHARACTERIZATION OF SOME LOW EXPLOSIVE RESIDUES BY ION CHROMATOGRAPHY" Terry L. Rudolph and Edward C. Bender FBI Laboratory, JEH Building, Washington, D. C. 20535

The FBI today is faced with over 200 terrorist and criminal bombings a year in the U.S. and its territories. Many of these bombings are committed with low explosives. For investigative purposes, there is a need to rapidly analyze bombing debris to determine the identity of the explosive used. X-ray powder diffraction is the most common technique used for this analysis, but this method lacks the sensitivity needed to do a thorough and complete job and, additionally, the instrumentation is very expensive. A method utilizing Ion Chromatography (IC) has been applied to both the qualitative and quantitative analysis of low explosive combustion residues. Several commercial and homemade explosive mixtures, such as black powder, fireworks mixtures, Pyrodex, and potassium chlorate/sugar are examined. Common anions found in explosive residues are analyzed using conductivity, electrochemical and variable wavelength UV detectors. The IC anion patterns found in the combustion residues of known explosives are then compared with the patterns of an unknown explosive. If the patterns are similar an identification of the explosive can often be made.

242 ON-LINE ION CHROMATOGRAPHIC ANALYSIS OF HIGH PURITY WATER SYSTEMS AT NUCLEAR POWER PLANTS. M.N. Robles and J.L. Simpson, General Electric Company, 175 Curtner Avenue, San Jose, CA 95125

The ionic content of power plant high purity water systems plays an important role in corrosion of plant components and the reliable production of electric power. Measurement of these ion concentrations, which are typically in the low microgram-per-liter region, is accomplished through the use of ion chromatography, sample concentration and on-line sampling. A description of the equipment, modified and automated, for application at several nuclear power plants is presented. The results obtained with these systems are described and include: sodium, chloride, and sulfate release from hideout locations during a controlled shutdown, transient detection, and a comparison of ion levels at three nuclear power plants.

243 SAMPLING AND ANALYSIS OF AIRBORNE INORGANIC PARTICULATES FROM SOUTHEASTERN LAS VEGAS BASIN. R. W. Davis. Stauffer Chemical Company, de Guigne Technical Center, 1200 South 47th Street, Richmond, CA 94804

High volume ambient air sampling was conducted at Henderson, Nevada, about ten miles south of Las Vegas. The study was intended to quantitate the particulate components collected during periods when a white cloud was visible near the industrial complex at Henderson, and if possible, to indicate which components contributed most heavily to the cloud. An earlier study showed that the particulates collected during cloud incidents were spheroidal in shape and 0.2 - 2.0 micrometers in diameter, and that they were largely water-soluble. The second study, the subject of this paper, was designed to quantitate the particulates' components and to investigate the possible presence of organic components. Analyses showed that the major water-soluble components were ammonium and various metallic chlorides, nitrates, and sulfates. The ratio of summed equivalents of anions to cations is quite close to unity. Finally, elemental carbon was shown to be present in the particulates. The procedures used to select optimum sampling periods and to collect the samples will be discussed, as will the specialized equipment used to ship samples without contamination. The techniques used to quantitate anions and cations are described.

244 USE OF THE I^2C APPROACH FOR ASSAY LEVEL ION CHROMATOGRAPHIC ANALYSIS. A.W. Fitchett, C. Pohl, and E.L. Johnson, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94086

Indirect Ion Chromatography (I^2C) is a new technology that has been licensed to Dionex Corporation. This approach (1) adds to the total capabilities of IC by extending analyses to the assay level. This paper will highlight the work that has been done with I^2C and will focus on the problems encountered with IC and SCIC at assay level concentrations.

1. H. Small and T.E. Miller, Jr., Anal. Chem, 54, 462 (1982).

245 THE MONITORING OF ELECTROLESS COPPER PLATING SOLUTIONS USING ION CHROMATOGRAPHIC EXCLUSION, L. C. Yeager and J. W. Basinger, Lockheed Missiles & Space Company, Inc., 0/48-50, Building 142, P.O. Box 504, Sunnyvale, CA 94086.

Replenishable electroless copper plating solutions are used in the manufacture of printed circuit boards. Replenishment is based on Cu/HCOH/NaOH content analyzed by standard titrimetric procedures. Such replenishment eventually becomes ineffective, and the bath must be discarded. As part of Lockheed's real time process control development project, a technique was devised for measurement of changes in concentration of the anionic species formate, acetate, tartrate, sulfate and carbonate. The goal was to determine whether changes in these parameters could be used to predict failure of the bath.

Mobile Phase Ion Chromatography (MPIC) and Ion Chromatographic Exclusion (ICE) were investigated as possible methods. It was found that ICE techniques were sufficient to determine the desired information. Carbonate was determined using water as eluent, and the other species with dilute HCl eluent. Shop baths and an experimental pilot line bath were monitored, and changes in bath performance correlated to changes in composition.

246 ANALYSIS OF PROGESTERONE AND METABOLITES FROM BREAST CANCER CELLS BY GC AND GC-MS Adrian W. Pike, Kathryn Horwitz, and P.V. Fennessey, University of Colorado School of Medicine, Denver, CO 80262.

Analysis of steroid hormones by gas chromatography and gas chromatography-mass spectrometry has proven to be an accurate and precise method for their determinations. We have utilized this method for investigating the metabolism of progesterone in breast cancer cell cultures containing highly specific progesterone receptors. Analysis of cell fractions after incubation with various precursors allows the rate of uptake from the media with subsequent cellular metabolism to be investigated. Our preliminary results indicate that progesterone is rapidly metabolized in vitro by a multicomponent enzyme system. The products of which are rapidly excreted back into the media. Structural elucidation of these products were confirmed by GC-MS. It is envisaged that this will demonstrate multicomponent analysis by GC-MS, as opposed to individual immunoassay, to be an important tool in the identification and quantitation of metabolites from isolated biological systems (i.e. cell cultures) as well as from physiological fluids (i.e. urine, plasma, saliva) as has been shown elsewhere.

247 APPLICATIONS OF AN RPN STACK-STRUCTURED ENVIRONMENT FOR GC/MS DATA. R.K. Latven, Hewlett-Packard Co., 3003 Scott Blvd., Santa Clara, CA 95050

Reverse Polish Notation (RPN) has been well characterized as an efficient environment for performing arithmetic operations in electronic calculators for more than a decade. However, its application for the manipulation of GC/MS data has recently been developed and is now available on a commercial GC/MS system. The last in-first out register stack (X,Y,Z,T) forms the structure by which ion chromatograms, mass spectra, and alphanumeric data are handled; this structure allows large amounts of spectral information to be handled with facility. In addition, many arithmetic and logical functions have been written which have not heretofore been used on data of this type. These RPN commands either control the register stack, operate on data in any one register, or perform arithmetic or logical operations on two registers together. In addition, a full device-independent graphics subsystem with alphanumeric overlay permits the presentation of these data in a variety of formats. The operation of the RPN stack and a description of its associated commands will be presented and examples of data so obtained will be shown.

248 HIGH RESOLUTION FAST ATOM BOMBARDMENT MASS SPECTROMETRY WITH A MULTICHANNEL ANALYSER. Keith L. Clay and R.C. Murphy, University of Colorado Medical Center, 4200 E. 9th Ave., Denver, CO 80262.

Fast atom bombardment (FAB) ionization of involatile or thermally labile molecules has greatly expanded the range of applicability of mass spectral analysis. One of the most powerful modes of mass spectral analysis, high resolution, has not been extensively exploited in combination with FAB primarily because of the low intensity of the signals generated with FAB. The approach we have taken to solve the problem of low signal intensity has been to use a multichannel analyser (MCA) in combination with a peak matching unit (PMU). Calibration of the MCA with the PMU and the use of standard compounds allows the determination of elemental composition on ions whose intensity would be insufficient for accurate measurement with the use of the PMU in the usual mode. Examples of the use of FAB for high resolution analysis of phospholipids, anthracene antibiotics and the peptidolipid leukotrienes will be presented.

249 ANALYSIS IN HUMAN METABOLISM OF STABLE ISOTOPES OF TRACE METALS, Celia Moynihan and P.V. Fennessey, University of Colorado School of Medicine, Denver, CO 80262.

Radio isotopes have been used with great success in studying metabolic processes in animals. However, they present ethical problems for human studies particularly when these studies include children and pregnant women. Stable isotopes are well suited for these studies. Currently, neutron activation, thermal ionization and direct probe mass spectrometry are being used to analyze stable isotope dilution during the metabolism of trace metals. The development of an analytical method which would utilize gas chromatography and mass spectrometry would be of a great advantage in studying the metabolism of trace metals in human subjects. The analysis of trace metals, which occur in physiological systems in the ppb range, has presented many difficult problems. We have been using gas chromatography as a means of separating chelates of iron, zinc and copper and we have employed mass spectrometry to analyze isotope ratios. We will present data and chromatograms of samples from biological sources using various chelators. These will be compared with samples separated by ion exchange chromatography chelated under optimum conditions and analyzed by fast atom bombardment mass spectrometry.

250 A REDUCED PRESSURE MICROWAVE PLASMA SOURCE FOR MASS SPECTROMETRIC ANALYSIS, S.K. MacLeod, L.R. Layman*, F.E. Licthe*, R.K. Skogerboe, Department of Chemistry, Colorado State University, Fort Collins, CO 80523, *U.S. Geological Survey, Box 25046, MS 928, Denver, CO 80225.

Recent research has focused upon the use of classical atomic emission plasmas as ion sources for the mass spectrometric analysis of aqueous solutions. These plasma sources provide the energy necessary for the desolvation and ionization of the nebulized solution. The majority of the work in this area has, with few exceptions, dealt with inductively coupled plasma (ICP) sources. While the ICP-MS systems exhibit very high sensitivity and isotopic ratio capabilities, these sources have a number of drawbacks due to the complex nature of the interface.

In this work, a reduced pressure microwave induced plasma (MIP) has been evaluated for its utility in the role of an ion source. The low flow rates and small thermal mass of the MIP simplify the MS interface to a considerable extent. Since the entire source may be sealed off from the atmosphere, a reduction in the background signals due to entrained nitrogen species is realized. The disadvantages of the ICP-MS system are overcome while maintaining the sensitivity and isotopic ratio capabilities inherent to plasma sources. Problems associated with desolvation in the microwave cavity are significantly reduced through the use of a fritted glass nebulizer.

During the course of the discussion, the efficacy of this approach will be demonstrated through the detailed examined of experimental results.

251 MEMORY EFFECTS IN MASS SPECTROMETRIC ANALYSIS OF VOLATILE METAL CHELATES, S.K. Macleod, R.K. Skogerboe, Department of Chemistry, Colorado State University, Fort Collins, CO 80523.

The existence of a condition in which the past set of events affects the present event in a stochastic process may be designated as a memory effect. The phenomenon has been well documented in regards to the use of volatile metal chelates for the determination of isotopic information by electron impact mass spectrometry. The effect manifests itself in the chelate studies by causing the isotopic abundance to be shifted in the direction of the last sample subjected to analysis. The problem has proven itself to be enigmatic and, for large scale studies, the results of the analyses are often questionable.

In this work, the mechanism of the effect is elucidated. Alternate ionization methods and mathematical modeling approaches are examined as possible solutions to the problem. In addition, novel ligands specifically designed to eliminate the memory effect are examined in detail.

252 **Abstract not available.**

253 MOMENT ANALYSIS OF ^{29}Si NMR SPECTRA FOR THE CHARACTERIZATION OF SHORT RANGE Si/Al ORDERING IN ZEOLITES. A. J. Vega, Central Research & Development Department, E. I. du Pont de Nemours & Company, Experimental Station, Wilmington, DE 19898.

Since the relative chemical shift of ^{29}Si in aluminosilicates is determined by nearest neighbor coordination, it is obvious that the information contained in a ^{29}Si spectrum can only be related to short-range ordering of the Al distribution in the framework. Long-range order can only be inferred in certain cases, e.g., when the Si:Al ratio is very close to 1. Hence, there is need for a quantitative formalism that describes the short-range order. This can be done in terms of the density (x) of the Al sites, the density (x_1) of Al-Al nearest-neighbor pairs, and the density (x_2) of Al-Si-Al linkages. Assuming that x_1=0 (Loewenstein's rule), we can directly determine x as well as x_2 from the first and second moments of the ^{29}Si spectra. Monte Carlo computer calculations will be described of randomized Al distributions in zeolite frameworks, under restrictions of Loewenstein's and Dempsey's rules. The method is applied to a hypothetical square planar lattice which allows the various Al distribution patterns to be visualized in simple displays, and to the zeolite X and Y framework the results of which will be compared with experimental data taken from the literature. It has been found that the x_2 parameter determines the homogeneity of the Al distribution in the framework.

254 ^{29}SI AND ^{27}AL HIGH FIELD MAS NMR STRUCTURAL STUDIES OF ZEOLITE CATALYSTS.

C.A. Fyfe, G.C. Gobbi and G.J. Kennedy, Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1, and (in part) R. Ozubko and W.J. Murphy. Research Department, Imperial Oil Ltd., Sarnia, Ontario, Canada N7T 7M1.

For many common Zeolites, five peaks are observed in the ^{29}Si NMR spectrum corresponding to the five local environments Si[4Al], Si[3Al, 1Si], Si[2Al, 2Si], Si[Al, 3Si] and Si[4Si] which fall within reasonably well defined shift ranges. The uses of these spectra and the corresponding ^{27}Al MAS NMR data for structure ellucidations and their limitations will be briefly reviewed. From a study of a number of highly siliceous zeolitic materials obtained by dealumination and of gem-quality minerals it will be shown that the substantial (5-10) ppm residual broadening in zeolite ^{29}Si MAS spectra is due, not to unaveraged dipolar interactions with the quadrupolar ^{27}Al nuclei present in the lattice, but to a combination of separate signals arising from crystallographically inequivalent silicon atoms in the unit cells and a distribution of environments for each such site due to second and further nearest neighbour interactions. In some cases, the shift dispersion due to site inequivalence may be of the same magnitude as the effect of aluminium in the first co-ordination sphere as in the case of Offretite and a detailed interpretation of the ^{29}Si MAS NMR data of this system will be presented. Comparison of the X-ray powder diffraction data of highly siliceous systems with the NMR chemical shifts yields a correlation which may be used for structural investigations of other systems.

The application of dealumination procedures to zeolite ZSM-5 converts its ^{29}Si MAS NMR spectrum to that previously found to be characteristic of the species Silicalite while no substantial changes occur in the X-Ray diffraction patterns or shifts of the ^{27}Al resonance, demonstrating directly the structural relationship between the two systems.

255 A COMPARATIVE STUDY OF THE PROPERTIES OF OFFRETITE AND ZSM-34

B. C. Gerstein and T. M. Apple
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and
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Offretite and ZSM-34, zeolites with nominally the same crystal structure, have been synthesized, and their catalytic behaviour toward conversion of methanol to alkenes has been determined. ZSM-34 is found to highly selective toward conversion to ethylene. The process of calcination of the zeolites during removal of the quaternary ammonium cation has been characterized by TGA, DSC and FTIR. Crystallinity was characterized by SEM. Acidity was monitored by pyridine absorption and FTIR. A variety of experiments on the NMR of protons at 220 MHz were performed on samples before, and after calcination. Spin counting is found to be diagnostic of crystal quality. The best samples of offretite were found to contain two populations of relatively immobile charge compensating protons, in sets separated by 6 and by 7 Å. Shielding anisotropies are found to be less than 15 ppm. Possible identities of the protons are discussed in light of this information.

256 Abstract not available.

257 Abstract not available.

258 ZERO FIELD NMR. D. P. Weitekamp, A. Bielecki, D. Zax, K. Zilm and A. Pines, Department of Chemistry, University of California, Berkeley, CA 94720

In polycrystalline samples, NMR 'powder spectra' are broad and much structural information is lost due to the orientational disorder. We describe Fourier transform NMR in zero magnetic field. With no preferred direction in space, all crystallites contribute equivalently and resolved dipolar splittings can be interpreted directly in terms of internuclear distances. This opens the possibility of molecular structure determination without the need for single crystals or oriented samples.

259 Abstract not available.

260 PHYSICAL AND CHEMICAL STATES OF SMALL MOLECULES ON DISPERSED NOBLE METAL SURFACES. A CP NMR STUDY. Holly B. Ragle and Jerome L. Ackerman, Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221.

In an attempt to study the motional states and reaction chemistry of adsorbate molecules in surface catalyzed reactions, we have prepared several silica-supported platinum catalysts and examined ^{13}C cross polarization NMR spectra of single carbon organic molecules adsorbed on the catalyst surfaces. On both unreactive clean silica and silica-supported platinum surfaces, the NMR spectra of methanol appear to show simultaneously populations of "liquid" and "solid" molecules, above and below the freezing point of the neat liquid, which are continuous functions of temperature. This is rationalized in terms of Resing's "apparent phase transition effect", which is here manifested as a gradual freezing out of the motionally narrowed features of the spectrum and the buildup of the powder pattern as temperature is lowered. It derives from a broad distribution of correlation times for methanol reorientation, which is in turn a reflection of the energetic heterogeneity of the interphase. With platinum present, adsorbed methane, showing an anomalous upfield chemical shift, is produced. We will present an analysis of the correlation time distribution, as well as a discussion of the chemistry of this system in relation to industrially important reactions such as Fischer-Tropsch synthesis.

261 PROBING PLATINUM SURFACES WITH NMR. Charles P. Slichter, Loomis Laboratory of Physics, University of Illinois at Urbana-Champaign 61801

In collaboration with Dr. John Sinfelt of the Exxon Research and Engineering Laboratory, my students and postdocs have been studying the NMR of small Pt particles dispersed on alumina. We have studied ^{195}Pt, ^{13}C and ^{1}H (of adsorbed molecules such as CO, C_2H_2) using spin echos. We measure NMR line shape, spin-lattice and spin-spin relaxation times from 77 K to 500 K. Extensive signal-averaging is needed. Studies of ^{195}Pt line shape versus Pt dispersion (fraction of Pt atoms on the surface of the particles) for dispersions ranging from 4% to 76% reveal a peak on the NMR from the surface Pt atoms. The position of the peak is characteristic of the surface coating, but is close to that of ^{195}Pt in diamagnetic compounds. By spin-echo double resonance between ^{195}Pt and ^{13}C, we resolve the detailed line shape of the surface ^{195}Pt on particles coated with ^{13}CO. The ^{13}CO resonance is strongly shifted down field from the ^{13}C resonance in diamagnetic compounds. Variation of spin-lattice relaxation time with temperature and static field, as well as a fit to the Korringa relation, show this to be a Knight shift. We suggest it arises from mixing of the CO orbitals with the metal wave functions. At elevated temperatures, CO diffusion on the surface is observed.
This work was supported by the U.S. Department of Energy, Division of Materials Science, under Contract DE-AC02-76ER01198.

262 MAR STUDIES OF CRYSTALLOGRAPHIC AND NMR PROPERTIES. Robin K. Harris, School of Chem. Sciences, Univ. of East Anglia, Norwich, NR4 7TJ England.

High resolution ^{13}C NMR investigations, using the CP/MAR technique, have been carried out for a range of metal acetates and formates, including several cases where more than one polymorphic form or more than one degree of hydration exists. Rapid MAR studies often give multiple peaks indicative of crystallographic inequivalences. Calcium and barium acetate monohydrates show four carbonyl resonances, and confirmatory X-ray evidence was obtained in the barium case. These compounds provide good test-cases for CP/MAR experiments since lines are very sharp. Slow MAR spectra allow shielding anisotropies to be obtained, and these may be discussed in relation to crystal structures, where known.

Slow MAR ^{13}C experiments on two phosphonium iodides, $(Me_2Ph_2P)^+I^-$ and $(Me_3PhP)^+I^-$ show peculiar intensities in the spinning sidebands, particularly when the non-quaternary suppression sequence is used. The sideband distribution can be attributed to the combination of (P,C) dipolar interactions, (P,C) scalar interactions and ^{13}C shielding anisotropy. Bandshape reconstruction techniques enable information on all three interactions to be recovered. The absolute sign of the (P,C) scalar interaction is obtained.

263 MAGNETIC RESONANCE STUDIES OF ACCEPTOR GRAPHITE INTERCALATION COMPOUNDS, H. A. Resing, G. R. Miller,* Larry Mattix, M. J. Moran,** and Jo Ann Milliken, Code 6120, Naval Research Laboratory, Washington, D. C.

NMR techniques have been used in graphite intercalation systems for chemical analysis and for determinations of structure, molecular dynamics, exchange kinetics, conductivity and electron concentration. We have been most interested in understanding the reaction

$$3AsF_5 + 2C_n \rightleftharpoons 2C_nAsF_6 + AsF_3 \qquad (1)$$

for which a single, extremely narrow ^{19}F NMR line is observed when AsF_5 reacts with graphite. In contrast, when the reaction

$$NO_2AsF_6(\text{in } CH_3NO_2) + C_n \rightarrow NO_2\uparrow + C_nAsF_6 \qquad (2)$$

is carried out, followed by addition of the stoichiometric amount of AsF_3, separate spectra for the AsF_6^- (a broad doublet) and for AsF_3 (a sharp 1:2:1 triplet) are observed, indicating that these two species do not exchange fluorine atoms, and suggesting that eq. (1) is not reversible. The AsF_3 triplet gives an order parameter for the molecular three fold axis with respect to the graphite c-axis. The triplet splitting for the protons of the co-intercalated CH_3NO_2 shows similarly that this molecule lies with its C-N bond vector normal to the c-axis. The hole concentration in these compounds has been determined by ESR at low frequencies and by carbon-13 NMR.
*University of Maryland **Westchester State University

264 ^{19}F MAS-NMR AND ^{19}F-^{31}P CP-MAS NMR OF FLUORIDATED HYDROXYAPATITE SURFACES James P. Yesinowski, Michael J. Mobley, and Donald J. White, The Procter & Gamble Company, Cincinnati, Ohio 45247.

High-field ^{19}F magic-angle spinning (MAS) NMR is a sensitive method for studying the fluoridation of hydroxyapatite surfaces exposed to aqueous fluoride. Bulk samples of fluoroapatite, $Ca_5F(PO_4)_3$, fluorohydroxyapatite solid-solutions, $Ca_5F_x(OH)_{1-x}(PO_4)_3$, and calcium fluoride exhibit characteristic ^{19}F MAS-NMR spectra at moderate spinning speeds. Thus, it is possible to identify these compounds when they occur at the surface of fluoride-treated hydroxyapatite. Solid-state transformations occurring at the surface can be monitored by ^{19}F MAS-NMR. Samples exposed to higher fluoride concentrations contain calcium fluoride as well as fluoroapatite; a Hahn spin echo can be used to quantitate the two components. Spin-lattice relaxation times suggest that the two components are in close contact at the atomic level. The MAS-NMR of ^{31}P would be expected to provide additional information about these surface samples. In order to selectively observe the ^{31}P NMR signals of apatitic phosphate groups at the surface (near ^{19}F nuclei), we have carried out the first ^{19}F-^{31}P cross-polarization experiments. Preliminary results of these experiments will be presented.

265 Abstract not available.

266 **Abstract not available.**

267 CPMAS-NMR STUDIES OF THE SYNTHESIS OF $(H^{13}C^{15}N)_x$ POLYMERS. R. A. McKay, Jacob Schaefer, and E. O. Stejskal, Physical Sciences Center, Monsanto Company, St. Louis, MO 63167 and Robert Ludicky and C. N. Matthews, Department of Chemistry, University of Illinois at Chicago, Chicago, IL 60680.

Hydrogen cyanide gas will react in the presence of amine to form a complex mixture of $(HCN)_x$ polymers. The structure of these polymers and the mechanism of their formation, especially the insoluble, higher molecular weight ones, is unclear. These analytically intractable systems are good subjects for ^{13}C- and ^{15}N-CPMAS study. Double-cross-polarization (DCP) NMR involves the sequential transfer of spin polarization from ^{1}H to ^{15}N to ^{13}C, followed by detection of ^{15}N under MAS conditions. The ^{15}N to ^{13}C transfer requires strong dipolar coupling between the spins and hence detects ^{13}C-^{15}N chemical bonds when compared with ^{15}N-CPMAS. Reactions of $H^{13}C^{15}N$ and $H^{12}C^{14}N$ or $H^{13}C^{14}N$ and $H^{12}C^{15}N$ to form $(HCN)_x$ can be examined with DCP to detect the making or breaking of ^{13}C-^{15}N bonds and to test hypotheses as to the routes to formation of these polymers.

268 FLUORINE-19 NMR INVESTIGATION OF BORON TRIFLUORIDE-MONOETHYLAMINE. Robert E. Smith and Fred Larsen.

Boron trifluoride monoethylamine (BF_3-MEA) is commonly used to accelerate the hardening of epoxy resins. In the past 20 years, there have been conflicting reports on the role of BF_3-MEA in accelerating the curing of epoxy resins. Fluorine-19 NMR should be a useful tool for clarifying the role of the BF_3-MEA. There are two features of the fluorine -19 NMR spectrum which provide useful information. The first is a quartet due to the BF_3. The chemical shift of this quartet tells us about the chemical enviroment of the BF_3. BF_3-MEA may dissociate, and then form a coordinate covalent bond with an epoxide oxygen from the resin. Alternatively, the BF_3-MEA may remain intact and only a hydrogen bond between the amine hydrogen (of MEA) and the epoxide oxygen be formed. The chemical shift of the quartet would be different by several ppm in these two cases. In fact, the spectrum of a room temperature mixture of BF_3-MEA and bis (N,N-di(2,3-epoxypropyl)-4-aminophenyl) methane (BDEAM) indicate that the BF_3-MEA remains intact. The second feature of the spectrum is a singlet due to BF_4-, which is formed by hydrolysis of BF_3-MEA. First, the size of this singlet is a measure of the degree of hydrolysis of BF_3-MEA. Second, the chemical shift of the BF_4- is a measure of the acidity of the system. This is indicated by titrating a HBF_4 solution with NaOH and observing an upfield movement of the singlet. This is important because some authors have proposed a mechanism whereby a proton is liberated by the BF_3-MEA. This would cause a downfield shift in the BF_4- singlet. However, this is not seen in the room temperature mixture of the BF_3-MEA plus BDEAM. Finally, a progress report will be given on fluorine-19 NMR spectra measured at 170°C during the course of the epoxy hardening.

269 IDENTIFY THAT TERPENE (WITH COMPUTER-ASSISTED NMR INTERPRETATION), M. Hagedorn, International Flavors and Fragrances, 1515 Hwy. 36, Union Beach, NJ 07735

To facilitate natural product structure determinations, a practical means of storing and accessing NMR data has been developed. Spectroscopic data on volatile terpenes were collected from the literature. Names, references and NMR data (ppm, multiplicity) were entered and linked into a database via a Data Retrieval System program (VAX/VMS). Additionally, eleven indexed characteristics describing NMR integrals in defined regions, molecular formulae, and functionality were evaluated and entered. The program permits rapid comparison of input index values with those in the data base. Specification of 7 indices generates a subset of ≤46 from 1050 structures; subsets can be further searched or displayed. Examples will be shown and extension to other compound classes discussed.

270 SOLID STATE ^{2}D-NMR STUDIES OF THE DYNAMICS OF $^+ND_3$ GROUPS IN AMINO ACIDS. Amikam Reuveni. University of Washington, Seattle, Washington 98195.

NMR studies of powders of partially and fully deuterated amino acids were performed over a wide range of temperatures. Lineshape analyses were made to distinguish between two types of motion of the $^+ND_3$ groups: rapid jumps between discrete equivalent sites and diffusional rotation (or jumps) between indistinguishable sites. Motional parameters were extracted by comparing the actual spectra with spectra simulated by using the appropriate motional models. A discussion of these results is made together with suggestions for extending these methods to studies of the motion of labeled acid side-chains in larger protein complexes.

271 EXPERIMENTS USING ^{33}S NMR, Peter S. Belton, I. Jane Cox*, and Robin K. Harris* Food Research Institute, Norwich. *University of East Anglia, Norwich.

Sulphur-33 (the only NMR active isotope of sulphur) has a low natural abundance, an average quadrupole moment and a small magnetogyric ratio. It resonates at 23.009 MHz in a field of 7.05 T.

Sulphur-33 signals can readily be obtained from species in which the sulphur is in a symmetrical environment. A spectrum can be obtained from tetramethylene sulphone (a neat liquid) in a single scan. The linewidth of the sulphate ion is less than 10 Hz in a 2M aqueous solution. The linewidth increases by a factor of 10 as the pH decreases from pH 5.26 to pH 0.6. The linewidth of tetramethyl sulphone is sensitive to the solvent - it varies from 16 Hz to 60 Hz for 2M solutions in acetone and water respectively. The chemical shift of a series of sulphones have been shown to vary by 6- ppm according to substitute.

In addition to sulphones and sulphates 'narrow' lines (i.e. those less than 1000 Hz wide) have been obtained from the thiosulphate ion, sulphonic acids and carbon disulphide. The sulphur environment in a number of compounds appears to be too asymmetric for lines to be observed using a high-power broadband probe in a Bruker CXP 300 spectrometer. Such compounds include methyl sodium sulphate and dimethyl sulphate; sodium sulphite, sulphides, sodium thiocyanate, sulphoxides and heavily substituted thiophenes.

272 Abstract not available.

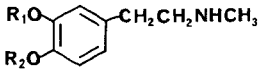
273 TWO-DIMENSIONAL ^{13}C NMR OF SOLIDS.* Arthur C. Lind and David A. Cornell.** McDonnell Douglas Research Laboratories, St. Louis, MO 63166.

Two-dimensional Fourier transform ^{13}C NMR spectroscopy has been used to study organic solids. Cross polarization, high power decoupling, and magic angle sample spinning were employed. The two dimensional spectra of naturally abundant carbon in a non-spinning sample contained cross peaks between non-equivalent carbons when a mixing time of 5 s was used. The cross peaks were not present when magic angle spinning or mixing times of 10 ms were used. The presence of the cross peaks is attributed to ^{13}C - ^{13}C dipolar coupling causing spin diffusion between the carbons. Two-dimensional techniques were applied to the study of molecular motion in polymers, and preliminary results are reported.

*This work was performed under the McDonnell Douglas Independent Research and Development program.
**Permanent address: Principia College, Elsah, IL 62028

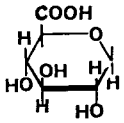
274 STRUCTURAL ASSIGNMENTS OF O-SULFATE ESTERS AND GLUCURONIDE METABOLITES OF EPININE BY HIGH FIELD PROTON NMR. George Y. Kuo, David B. Staiger, and Bruce Y-H Hwang. Smith Kline & French Laboratories, 1500 Spring Garden Street, Philadelphia, PA 19101.

We have studied the high field (400 MH_z) proton NMR spectra of epinine (I), 3-O-methylepinine (II), epinine 3-O-sulfate (III) and epinine 4-O-sulfate (IV) in order to determine the site of metabolic sulfation and glucuronidation on I and II. The sulfate ester of epinine (SEE) is the major metabolite isolated from dog urine. Both epinine glucuronide (EG) and 3-O-methylepinine glucuronide (MEG) are major metabolites in rat bile. Compounds I, II, III, and IV are synthetic samples. High field proton NMR data indicate that SEE is epinine 3-O-sulfate rather than epinine 4-O-sulfate. Glucuronidation of EG and MEG occurred at the 4-hydroxy group. Hence, the structures of EG and MEG are assigned to V and VI, respectively. Substitution of a sulfo ($HOSO_2$-) or a glucuronyl group on the hydroxy (-OH) group shifts the ortho and para-protons 0.3~0.4 ppm downfield. Little or no effect was observed on the metaprotons.



I, R_1=R_2=H
II, R_1=CH_3, R_2=H
III, R_1=SO_3H, R_2=H
IV, R_1=H, R_2=SO_3H
V, R_1=H, R_2=Glu
VI, R_1=CH_3, R_2=Glu

Glu=



VARIABLE-TEMPERATURE ^{13}C SOLID STATE NMR AS A PROBE OF POLYCARBONATE-DILUENT INTERACTIONS. Laurence A. Belfiore, Dept. of Agricultural & Chemical Engr., Colorado State University, Fort Collins, Colorado 80523 and Stuart L. Cooper,
275 Dept. of Chemical Engr., University of Wisconsin, Madison, Wisconsin 53706.

The results of previous NMR $T_{1\rho}$ experiments indicate that the low molecular weight additive, dibutylphthalate (DBP), alters the mid-kilohertz mobility of glassy bisphenol-A polycarbonate (BPAPC) in a cooperative manner at ambient temperature. The purpose of this contribution was to investigate the effect of plasticization on BPAPC chain motions over a wide range of temperature. High-resolution carbon-13 $T_{1\rho}$ experiments between -95°C and 23°C[1] reveal that phenyl ring oscillations in the polymer-diluent blend are on the long correlation-time side of the 28 kHz minimum. In contrast, the aliphatic motions dominated by methyl group rotation are faster than 28 kHz in both the undiluted polymer and the blend. In the presence of 22 wt.% DBP, Arrhenius activation energies of 560 and 510 cal/mole were calculated for the protonated and nonprontonated aromatic carbons, respectively, in BPAPC. The surprisingly low values of the activation energies agree favorably with the conformational calculations of Tonelli[2] on an isolated BPAPC chain. This suggests that the hindrance to phenyl ring motion, as probed by NMR $T_{1\rho}$, is primarily intramolecular in origin. In contrast, dynamic mechanical and dielectric activation energies of 8-14 kcal/mole have been observed for mid-kilohertz motions in BPAPC and BPAPC-diluent blends below ambient temperature. Hence, one might question the degree to which NMR and mechanical relaxation measurements are correlated.

[1] Courtesy of Dr. J. R. Lyerla, IBM Research Laboratories, San Jose, California.
[2] A. E. Tonelli, Macromolecules, 5, 558 (1972).

276 NMR OUTSIDE THE RF COIL AND OUTSIDE THE MAGNET?

Alan Rath*, Stephen B. W. Roeder*, and Eiichi Fukushima+

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Computer modelling of magnetic fields demonstrates the feasibility of doing nmr in the region outside of two, nested solenoids with opposite polarities. Homogeneity is greatly enhanced by a second pair of such coils, permitting in principle, topical nmr of a human torso without placing the patient inside a solenoid. Coil designs for nmr rf coils will also be presented.

277 THE STRUCTURE OF AMORPHOUS FILMS CONTAINING TRI-P-TOLYLAMINE AND BISPHENOL-A-POLYCARBONATE AS DETERMINED BY HIGH-RESOLUTION ^{13}C NMR OF PARTIALLY DEUTERATED SAMPLES.
J. M. Hewitt, P. M. Henrichs, M. Scozzafava, R. P. Scaringe, M. Linder and L. J. Sorriero, Research Laboratories, Eastman Kodak Company, Rochester, NY 14650

Polymer properties can be modified dramatically when they are blended with various small molecules. We have been exploring the usefulness of high-resolution ^{13}C NMR to learn something about the spatial arrangement and specific interactions of such small molecules in an amorphous polymer film. When one of the components is deuterated, intermolecular cross-polarization can be made to occur from those molecules containing protons to those containing no protons (deuterated). The rate of the transfer of magnetization to a particular carbon during cross-polarization is inversely proportional to the square of the dipolar coupling between the protons and the carbon. Thus, the rate should be a sensitive measure of interatomic distance. In practice, large differences in cross-polarization rates have not been found, but we have still been able to obtain details on the structure of a blend of tri-p-tolylamine and bisphenol-A-polycarbonate with this technique.

278 A ^{2}H NMR ANALYSIS OF THE MOLECULAR ORIGIN OF THERMAL TRANSITIONS IN POLYCARBONATES
Patrick B. Smith, Robert A. Bubeck and Steven E. Bales, Analytical Laboratory, Dow Chemical Company, Midland, MI 48640

Dynamic mechanical spectroscopy provides an excellent device by which to study the thermal behavior of solid polymers on a macroscopic scale. However, the assignment of specific molecular motions which give rise to these relaxations is often tenuous but necessary in order to develop insight into the relationship between the physical performance of a polymer and its molecular architecture.

This paper presents the characterization of the thermal relaxations in Bisphenol-A (BA) polycarbonate and BA-terephthalate polyestercarbonate by solid state, wideline ^{1}H and ^{2}H NMR spectroscopy. This study utilized deuterium labeled analogues of the polymers in order to observe the motions of specific functional groups. The lineshape and quadrupole splitting of the ensuing powder patterns were characteristic of both the type and frequency of motion present as a function of temperature. The γ and β relaxations in these systems were assigned to specific molecular motions with the spectra obtained.

279 SOLUTION AND SOLID STATE NMR STUDIES OF POLYCARBONATES AND POLYSULFONES.
Philip Klein, Yang-Taur Shieh, David Cory and William M. Ritchey, Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.

Motions about phenylene oxide linkages in the title compounds were studied by solution and solid state ^{13}C NMR. Variations in T_1, T_2 and noe's were measured with changes in temperature and concentration. In solid state CP/MAS studies T_1, T_2 and conformational changes about the alpha ring carbon are observed as a function of temperature, at various concentrations of plasticizer. Protonated dephasins experiments were also employed. The results are compared to dynamic mechanical property measurements.

280 Abstract not available.

281 Abstract not available.

282 Abstract not available.

283 Abstract not available.

284 NMR OF VIRUSES, S.J. Opella, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104

Recent developments in the study of viruses by NMR spectroscopy will be discussed using several filamentous viruses as examples. Solid state NMR methods make available the details of spin interactions for analysis. The comparison of properties of unoriented and oriented samples, makes it possible to separate dynamical and structural parameters.

285 NMR AND SPECTROSCOPIC STUDIES OF THE METAL ION BINDING SITES OF α-LACTALBUMIN by Lawrence J. Berliner, Kentaro Murakami and Hiroyasu Nishikawa, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210, U.S.A.

Mammalian milk α-lactalbumins all contain a unique, very high affinity Ca(II) site which is also specific for several other divalent (Mn, Mg) and trivalent lanthanide cations. The binding of metal to the apo-protein induces a conformational change which is characterized by distinct changes in the proton NMR and intrinsic fluorescence emission. A strong indication of the nature of this site was learned from the chemical shift of ^{113}Cd substituted protein. When binding the cations Zn(II), Al(III), Co(II) or Cu(II), the protein apparently shifts toward the "apo-conformation", expelling Ca(II) from the calcium site. The zinc and calcium sites are competitive but distinct.

Supported by NSF and NIH grants.

286 ORIENTATION DEPENDENT NMR AND EPR SPECTRA OF PLANT LEAVES. Douglas C. McCain, Dept. of Chemistry, Univ. of Southern Miss., Hattiesburg, MS 39406 and John L. Markley, Dept. of Chemistry, Purdue Univ., W. Lafayette, IN 47907

All that can be seen in the ^{1}H NMR spectrum of a typical plant leaf is one broad signal from the water protons; the EPR spectrum usually shows organic radicals in the photosynthetic system as well as manganous ions. Most leaves have isotropic NMR and EPR spectra; i.e., results are independent of orientation except for predictable NMR shifts due to sample geometry, and EPR spectra are usually equivalent to those of a "powder" sample. However, in certain plant species the NMR spectrum may be resolved into two or three broad lines with chemical shift values which depend on the angle between the applied field and a vector normal to the leaf surface. Each NMR line has its own characteristic T_1 and T_2 relaxation times. Such NMR spectra are species specific; different species show significantly different patterns. EPR spectra of these leaves also show orientation dependence much like that of a single crystal. Chloroplasts are subcellular organelles with an internal structure composed of parallel stacks of planar photosynthetic membranes; as such they are inherently anisotropic. In green leaves, chloroplasts contain a significant fraction of the total water and most of the radicals and ions detected by EPR. We interpret our results as evidence of nonrandom chloroplast alignment. Calculations based on this model reproduce the details of our NMR and EPR spectra. Anisotropic NMR spectra can be used for biological studies of water stress or low temperature acclimation in leaves. EPR can be used to measure properties of the photosynthetic system, e.g. the alignment of radicals or ions with respect to the plane of the thylakoid membrane.

287 COPPER AND NICKEL BINDING TO SERUM ALBUMINS BY CHLORIDE NMR. P. Mohanakrishnan, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2; R.H. Cox, Philip Morris Research Center, Richmond, Virginia 23261 and C.F. Chignell, Lab Environ. Biophys., NIEHS, P.O. Box 12233, Research Triangle Park, NC 27709.

The binding of metal ions Cu^{2+} and Ni^{2+} to bovine, dog and human serum albumins was studied using ^{35}Cl NMR at 7.794 MHz on a Varian FT-80 spectrometer operating in the pulsed Fourier transform mode. The albumin solutions (a few μM in concentration) were titrated against the metal ions and line widths of chloride nmr signals were measured. The experimental was 5.4 for Cu^{2+} titrations and 10.4 for Ni^{2+} titrations. From the plots of the increase in line widths as a function of the ratio of concentrations of the metal ions and albumins, the number of primary copper sites were estimated to be between 1 and 2 for HSA, above 3 for BSA and above 6 for DSA. An identical number of Ni^{2+} primary sites were obtained for these albumins. This result, in comparison with previous studies, seems to indicate that both metal ions have the same primary sites on albumins. From the initial slopes of the plots it appears that the primary Cu^{2+} and Ni^{2+} sites of DSA are quite different from those of HSA and BSA. The estimates for primary Cu^{2+} sites and the trend in affinity for Cu^{2+} and Ni^{2+} are in agreement with previous studies.

288 RAMAN INVESTIGATION OF AQUEOUS ZINC BROMIDE COMPLEXES. Charles A. Cody, Bruce K. Faulseit, William W. Reichert, NL Chemicals, Box 700, Hightstown, NJ, 08520 and R. Keith Darlington, NL Baroid, Box 1675, Houston, TX 77251

Raman spectroscopy has been used to investigate $(ZnBr_x)^{2-x}$ complexes in aqueous solutions. The influence of Zn^{+2}/Br^- ratio, addition of mono and divalent bromide salts and salt concentration on zinc bromide complexes will be discussed. Computer techniques have been used to resolve overlapping Raman bands and to integrate band intensities. Polarization studies of the Raman bands provide information concerning the structures of the zinc bromide complexes.

289 THE USE OF RAMAN AND MICRORAMA TECHNIQUES IN THE STUDY OF KEVLAR 49 DEGRADATION Fred P. Milanovich, Steven Miller, Tomas Hirschfeld, Lawrence Livermore National Laboratory, Livermore, CA 94550. Stan M. Klainer, ST&E Technical Services, Inc., 20 Belinda Ct., San Ramon, CA 94583.

Extensive studies have been conducted regarding the mechanical behavior of poly (p-phenylene terephthalamide) fiber (known commercially as Kevlar 49). Of particular interest is the reduction of mechanical strength when the fiber has been exposed to heat; stress; radiation and; most importantly, epoxies (as in composites). We have used vibrational spectroscopy (Raman & microRaman) to probe for chemical changes induced by these exposures. To first order, ordinary Raman indicates that no large-scale chemical degradation is occurring. However, observed, subtle spectral changes are sufficient to propose a model for Kevlar failure under stress. Data are presented to support microcrystalline structure changes prior to failure. To assess the extent of these microscopic chemical changes, we employed a microRaman spectrometer. The spectrometer, which we describe here, has 1-μ resolution and high-collection efficiency. Fibers, both composite and bare, were observed both parallel and perpendicular to the axis. No major chemical changes were observed at the fiber-epoxy interface. However, subtle changes were again obtained, and they lend support to conclusions reached with ordinary Raman scattering.

*Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract number W-7405-Eng-48.

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RAMAN SPECTRA OF MICROSAMPLES OBTAINED WITH AN INTENSIFIED DIODE ARRAY SPECTROGRAPH

Donald O. Landon and Dianna G. Jones, Tracor Northern, Inc., 2551 W. Beltline Hwy., Middleton, Wisconsin 53562; and Edgar S. Etz, Center for Analytical Chemistry of the National Measurement Laboratory, U. S. National Bureau of Standards, Washington, DC 20234

Since the efficiency of spontaneous Raman scattering is low, the signals measured are usually of low intensity and the advantages of obtaining the entire Raman spectrum simultaneously are obvious. When taking Raman spectra of microsamples, particularly microparticles, the optical power incident upon the sample must be limited to relatively low values to avoid sample degradation. Obtaining the entire Raman spectrum in one shot is a must. We will describe experiments performed on a Raman triple spectrograph constructed specifcally for microsample analysis. Well-known standard scatterers including napthalene, polystyrene and ZrO_2 are used to compare the performance of the system with wavelength scanning systems. Of particular interest is a comparison of various state-of-the-art detectors, such as SIT vidicons and intensified silicon photodiode arrays.

291 LOW FREQUENCY DYE LASER RAMAN SPECTROSCOPY. James E. Griffiths, Bell Laboratories, Inc., Murray Hill, New Jersey, 07974.

Dye lasers are used to excite Raman spectra in difficult materials or in situations where resonance enhancement is required to overcome the obstacle of samples with low Raman cross-sections or extremely low concentrations. Despite outstanding successes in studies of such materials, however, there are insidious limitations in the use of a dye laser as an excitation source which originate in the optical properties of the laser and of the dye itself. Often, the consequence is to deny to the experimentalist access to the low frequency region of the Raman spectrum. This is especially true for samples that are subjectively labelled difficult. The problem may in fact lie with the laser and not with the sample. Various aspects of dye lasers will be reviewed briefly followed by a detailed discussion of the available ways one may gain access to the low frequency Raman bands. These include the use of intracavity optical elements, extracavity filters, prisms, grating monochromators, etalons and variable free spectral range Fabry Perot interferometers. It will be evident that the latter is the apparatus of choice to reduce dye laser fluorescence. Specific materials will be discussed, notably deeply colored non crystalline selenium glass, whose microscopic structure and concommitant properties have been sources of controversy for several years.

292 TRACE ANALYSIS OF MOISTURE IN INTEGRATED CIRCUIT PACKAGES USING DERIVATIVE DIODE LASER SPECTROSCOPY J. A. Mucha Bell Laboratories, 600 Mountain Avenue Murray Hill, New Jersey 07974

Derivative infrared diode laser spectroscopy has been used for the rapid and precise ($\pm$50 ppm_v) determination of trace ($\geq$50 ppm_v) moisture in small (10-100uL) samples of gas as they expand into an evacuated absorption cell. Adsorption/desorption of the analyte is the most serious potential source of error in the measurement; however, the application of time-resolved (resolution $\leq$10 msec) techniques permits accurate analyses in the presence of these dynamic processes. The experimental method and a simple model which accurately reproduces the concentration-time behavior observed during analysis are presented which permits the analyst to ensure the accuracy of any given measurement or detect and correct erroneous ones. The method has been applied to the determination of moisture in hermetically sealed integrated circuit (IC) packages and is shown to be capable of determining both gaseous and adsorbed moisture within the samples. Results for packages sealed under controlled moisture conditions exhibit large discrepancies when compared to those obtained by mass spectrometry (MIL STD Method 1018.2). Potential sources of the deviations are discussed along with advantages of this new method for IC moisture measurements.

293 ORIENTED POLYCRYSTALLINE FILMS FOR INFRARED SPECTROSCOPIC STUDIES. James M. Landry and J. E. Katon, Department of Chemistry, Miami University, Oxford, Ohio 45056.

Polarized infrared and Raman spectra have been shown to be useful in elucidating crystal structures. For over fifteen years, it has been known that polarized infrared spectra could be obtained from oriented polycrystalline films of organic compounds grown by cooling the melt between alkali halide windows. Although this technique has proved to be useful, the types of compounds and window materials examined have been limited. We now wish to report the formation of oriented polycrystalline films of inorganic and organometallic compounds, also grown from the melt. These films were grown on various window materials such as alkali and alkaline earth metal halides, silver chloride, Irtran-2, quartz and teflon. It has been found that portions of these films prepared on teflon can be removed and their polarized infrared spectra studied on any other window substrate. Current understanding of oriented polycrystalline film growth will be presented including aspects such as polymorphism and attainment of different crystal faces.

294 IR STUDY OF AMORPHOUS SILICON NITRIDE FILMS, J. P. Luongo, Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974.

Deposited films of amorphous silicon nitride which are used for surface protection or as an insulating interlayer in microelectronic devices have been studied by IR. The observed changes in the vibrational frequency location of the broad infrared Si-N antisymmetrical stretching absorption in the spectra of various plasma deposited silicon nitride films indicate the formation and inclusion of impurities within the silicon nitride network. The deposited films are composed principally of amorphous silicon nitride but small amounts of hydrogen, oxygen, and nitrogen containing moieties were found which contributed to the displacement of the Si-N absorption. The associated functional groups were identified as Si-H, NH, SiO_x, and $Si-O-N_x$. IR was used to quantitatively measure the hydrogen containing impurities. The method provides a means of identifying and correlating impurity levels with properties of the films.

295 SOME PRACTICAL APPLICATIONS OF INFRARED SPECTROSCOPY TO TEXTILES
Prof. Gultekin Celikiz, Philadelphia College of Textiles and Science, Henry Avenue and School House Lane, Philadelphia, PA 19144.

Infrared spectroscopy has become an important analytical tool in the identification of finishes and fibers. Finishes are extracted from fabrics by a standard American Association of Textile Chemists and Colorists AATCC) method. Spectra of the extracted chemical finishes are obtained and from the functional groups present the finishes are identified. Some classes of finishes extracted are:

natural and synthetic resins
softeners
polyethylene
polystyrene
urea

296 IR SPECTROSCOPY OF COMPLEX CONVERSION COATINGS. Dr. Max Kronstein, Joined Chemistry Department, Manhattan College/College of Mount St. Vincent, 4513 Manhattan College Parkway, Riverdale, New York 10471.

In close cooperation between the chemist, the chemical engineer and the IR spectroscopist, this method establishes the chemical processes in their important aspects. This researcher has shown some years ago how progressing polymerization can so be followed. Important production steps and varying conditions result in spectrum changes whereby it is to be established in what particular wavelengths these changes are to be found. This paper studies, in particular, the development and effectiveness of complex conversion coatings, based on reactions between organic polymers with modified metal oxides, which convert precleaned metal surfaces to a non-metallic state, as a base for protective coatings. After establishing the spectrum of the polymer ligand, its entry into the complex compositions can be determined under varying compositions, operating conditions and applications. The entry of additional metal groupings appears at given wavelength ranges. When the solutions are studied in sufficient concentrations to allow the expected variations to appear clearly, the most desirable compositions can be determined. In particular the interface between the metal surface and the applied conversion coatings can be studied systematically in order to establish the effectiveness of the application.

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CIRCULAR VARIABLE FILTER CHARACTERIZATION FOR SIMULATING INDUSTRIAL IR ANALYZER RESPONSE, R.B. Lam, A.A.D'Alessio, S. Day, The Foxboro Company, 140 Water Street, South Norwalk, Connecticut 06856

Interference filters are widely used for wavelength selection in infrared industrial analyzers for ambient air and process stream monitoring. The robustness of filter monochromators allows construction of rugged analyzers that retain reliability in harsh industrial environments. However, interference filters have relatively low resolution compared to other dispersive or Fourier transform IR instruments. For rapid assessment of industrial application feasibility, the effects of resolution on sensitivity, wavelength selection and interference rejection must be known.

This paper describes a mathematical model of filter-based IR analyzer response which can be used to rapidly predict applications feasibility from stored spectral data, without the need for repeated experimentation. The model is based on average bandwidth data collected from a large cross-section of interference filters. Filter band shape models are convoluted with high-resolution FTIR spectra to simulate filter instrument response, taking into account source, detector, optical and temperature effects. Comparisons of the model with experimental data are presented and use of the model for typical application problems is explained.

298 UPGRADING OF INFRARED GAS ANALYZERS FOR PROCESS CONTROL
DAN F. MANKA, Consultant, 1109 Lancaster Avenue, Pittsburgh, Pennsylvania 15218

A preferred method for continuously analyzing process gases is by infrared analyzers. However, stability of the analyzers is affected by variation in (1) gas flow; (2) gas pressure; (3) gas temperature; (4) analyzer temperature; and (5) atmospheric pressure. This paper will discuss a simple method with absolute pressure regulators which stabilizes the analyzers so that calibration remains within $\pm$ 0.1% in every 8-hour calibration period. Occasionally, in the analyses of gases from a furnace, a very small amount of a fine powder is carried through to the analyzer. This powder is carried into the analyzer. The powder adsorbs CO and CO_2 so that calibration may take up to one hour to reach the correct composition value. This powder generally forms when the brick lining of the furnace is old and the furnace needs to be relined. A method for preventing the adsorption of CO and CO_2 by the powder will be discussed. These methods are now located in analysis of CO and CO_2 in blast furnace top gas and in the basic oxygen furnace.

299 INFRARED STUDIES ON THE THERMAL DEGRADATION OF POLY (D_3-, 1-^{13}C, AND ^{15}N-ACRYLONITRILES) J. J. Rafalko, Celanese Research Company 86 Morris Ave., Summit, N.J. 07901

Poly (D_3-, 1-^{13}C-, and ^{15}N- acrylonitriles) and $^{18}O_2$ have been used to assign the infrared spectra of the thermal degradation products of polyacrylonitrile. The isotopic data and elemental analyses show that the degradation products can be made free of oxygen. Polyacrylonitrile is initially converted to substituted imines as evidenced by a 1582 cm^{-1} band. Aromatic heterocycles are formed by the elimination of HCN or NH_3. Enamines are stabilized by being adjacent to these heterocycles or they are formed by the elimination of NH_3 from two adjacent unsubstituted imines. Initially a 1616 cm^{-1} band results from enamines and unsubstituted imines. The enamines' contribution to the band increases relative to the unsubstituted imines' contribution as the reaction proceeds.

300 THE TRANSFORMATION MATRICES OF SYMMETRY OPERATIONS USED IN INFRARED SPECTROSCOPY Philip G. Bourne Scott Paper Co. Scott Plaza, Philadelphia, PA 19113

The construction of transformation matrices of symmetry operations is described, along with their use in Infrared Spectroscopy. The simplicity of determining point groups and molecular symmetry using matrices is demonstrated. The standard mathematics of the matrix system allows for easier understanding and handling than does the spacial manipulations of symmetry operations.

301 VIBRATIONAL SPECTRA AND CONFORMATIONS OF SUBSTITUTED CYCLOPROPANE DERIVATIVES. V.F. Kalasinsky, Y.F. Yen, and C.S. Murrey, Department of Chemistry, Mississippi State University, Mississippi State, MS 39762 and Department of Chemistry, University of Missouri, Kansas City, MO 64110.

The infrared and Raman spectra of (cyanomethyl)cyclopropane, (iodomethyl)cyclopropane, epiiodohydrin, and dicyclopropylmethane have been studied in the fluid and solid phases. (Iodomethyl)cyclopropane exists in a gauche conformation, and no evidence of a second conformer was found. Each of the other molecules exhibits a conformational equilibrium in the fluid states while a single conformer exists in the crystalline solid state. Epiiodohydrin (iodomethyloxirane) has been found to exist as at least two conformations in the liquid state. The gauche-1 and gauche-2 conformations are separated by 0.50 ± 0.10 kcal/mole with the former being the more stable. In the solid state, the Raman spectrum exhibits bands for the gauche-1 conformer but previously reported infrared spectra indicate that either form may exist in the solid state. A series of doublets exist in the Raman spectrum of liquid (cyanomethyl)cyclopropane and the temperature dependence of the line intensities is consistent with an energy difference of 0.70 ± 0.10 kcal/mole with the gauche conformer more stable than the cis. In dicyclopropylmethane, at least two conformers exist in the liquid state, and these have been identified as gauche-gauche conformers exhibiting C_2 and C_s molecular symmetries. The former was determined to be 0.93 ± 0.10 kcal/mole more stable than the latter. Comparisons with similar molecules and a discussion of the conformer equilibria will be given.

302 Infrared Photoacoustic and Diffuse Reflectance Spectroscopy of Absorbed Pesticides. D. J. Gerson, IBM Instruments, Inc., Orchard Park, Danbury, CT and W. G. Fately, Department of Chemistry, Kansas State University, Manhattan, KS.

Infrared photoacoustic and diffuse reflectance spectroscopy have been used to examine molecules absorbed onto surfaces of catalysts, polymers and glasses (Gerson, Wong, and Casper, Amer. Lab, (1983) in press). In this paper, these techniques have been used to examine the absorption of Atrazine™ on soil. The spectra of the absorbed pesticide at several ppm loadings on soil have been recorded. The difference spectra (absorbed pesticide - native soil) reveal small concentration dependent frequency shifts in bands associated with the pesticide. The possible sources of these shifts will be discussed.

303 COMPUTERIZED INFRARED IDENTIFICATION (CIRID) PROGRAM IN PHARMACEUTICAL CONTROL LABORATORY, R.S. Chao, D.A. Hatzenbuhler, R.G. Richman, J.M. Winkworth and A.M. Richter, Control Spectroscopy R&D, The Upjohn Company, Kalamazoo, MI 49001

Infrared spectroscopy has been widely accepted and used for qualitative identification in the pharmaceutical industry. Consistent with regulatory criteria on infrared identification, a unique Computerized Infrared Identification (CIRID) program developed in our Control laboratory is described. The approach involves spectral subtraction between sample and a predetermined reference on a region-by-region basis, and the measured spectral residuals are normalized and summed to provide a "comparison index" for judging the match of the two spectra. If the comparison index is sufficiently small, a positive identification is concluded. If the index exceeds an alert limit, the computer would alert the operator for subsequent actions. Results of a feasibility study and the implementation which include 1) instrument optimization, 2) lot-to-lot reproducibility, 3) discrimination of different compounds and 4) establishment of comparison limit will be presented.

304 Abstract not available.

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305 APPLIED SURFACE ANALYSIS - PRESENT AND FUTURE, N. S. McIntyre, Surface Science Western The University of Western Ontario, P+A Building, 101, London, Ontario, Canada N6A 3K7

The role of the surface analyst in an industrial setting has become particularly rewarding in the past several years. Fast-breaking technological developments have demanded analytical techniques and procedures which are as exacting as the processes and materials which they are attempting to define. At present, the best-known example of this is in the semiconductor industries, where surface analysts have concentrated on developing elemental detection sensitivities and spacial resolution adequate to characterize micron-size structures. Thus, Secondary Ion Mass Spectrometry (SIMS) and, to a lesser extent, Rutherford Backscattering Spectrometry (RBS) have gone through a period of very rapid development. In the future, an increased percentage of new analytical developments is predicted to come from laboratories involved in characterizing the role of chemical species in surface protection, adhesion, and corrosion. Techniques such as X-ray Photoelectron Spectroscopy and high resolution Auger Electron Spectroscopy already are undergoing a new period of growth, with much of the interest coming from the chemical industries. In addition to the electron and ion optical techniques which have become well-established over the past ten years, there has been recent progress in adapting optical spectroscopic methods to the analysis of applied problems. Photoacoustic Spectroscopy (PAS) is one such technique, and examples of PAS studies from the author's laboratory are cited.

306 QUANTITATIVE ASPECTS OF SIMS AS A DEPTH PROFILING TECHNIQUE: SOME APPLICATIONS IN ENERGY RESEARCH PROGRAMS.* W. H. Christie, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830.

One of the biggest problems encountered in using SIMS as a quantitative depth profiling technique is the inability to accurately calibrate observed ion yields as a function of actual concentration of a species in a particular matrix. Ion implantation standards offer an easy means for accurately determining the relationship between observed ion yields and actual concentration of a given species in most solid matrices. We have used these materials in a calibration technique for quantitative depth profiling studies. The application of these methods in analyzing GaAs photovoltaic devices will be discussed. Another technique used in our laboratory for quantifying SIMS data is the relative sensitivity factor. This method and an improved version, the indexed sensitivity factor, will be described. The application of indexed sensitivity factors will be discussed in the analysis of thermocouple failure and in the depth profiling of oxide films grown on Incoloy-800 heat exchanger surfaces.

*Research sponsored by the U. S. Department of Energy, Division of Basic Energy Sciences, under Contract #W-7405-eng-26 with the Union Carbide Corporation.

307 RUTHERFORD BACKSCATTERING ANALYSIS FOR ELECTRONICS MATERIALS CHARACTERIZATION Michael D. Strathman, Charles Evans & Associates, 1670 S. Amphlett Blvd., Suite 120, San Mateo, CA 94402

This paper will cover two major topics: 1) an overview of Rutherford Backscattering Spectrometry (RBS) and 2) a discussion of the applicstions of RBS to the analysis of electronic materials. The overview will give a basic understanding of the fundamentals of RBS including kinematics, energy loss, sensitivity, thickness measurement and channeling. The applications portion will cover topics including dielectrics, metalization, impurities, and crystaline quality. Under dielectrics the examples will be the measurement of stoichimetry and thickness of very gate oxides and the quantitation of phosphorus in phosphosilicate glass. The metalization applications will include the measurement of Al density and the characterization of refractory metal silicides. The application of RBS to the detection of surface impurites will be demonstrated for the case of residual impurities left after wafer cleaning. The final topic, channeling, will cover the application of RBS in measuring lateral crystal quality in advanced semiconductor materials.

308 DESIGN CONSIDERATIONS FOR A DEDICATED THIN FILM ANALYZER AUGER SYSTEM, Robert L. Gerlach, Perkin-Elmer Corporation, Physical Electronics Division, 6509 Flying Cloud Drive, Eden Prairie, Minnesota 55344

With increased acceptance and usage of surface analysis instrumentation in app science laboratories, there is a need for high performance, inexpensive, dedicated instruments. For example, sophisticated Scanning Auger Microscopes (SAMS) are bein used not only for high resolution work but also are burdened by low spatial resolut depth profiling studies. A dedicated Thin Film Analyzer (TFA) is desireable in thes and other situations. In this paper, design criteria are presented for a TFA with d consideration for performance, operator friendliness, simplicity, and cost.

309 CRISS, An NSF Regional Instrumentation Facility and Synchrotron Radiation Facilitie G.J. Lapeyre, J.R. Anderson, and D.J. Frankel, Department of Physics, Montana State University, Bozeman, Montana 59717

The Center for Research in Surface Science and Submicron Analysis (CRISS) is a user facility for scientific research. The operating characteristics of the instruments and facility management policies will be described. Of the two major instrument systems, one is a high resolution (500 Å beam) scanning Auger microprobe and the other one integrates an X-ray photoelectron spectrometer (ESCA) and high-resolution (about 6 meV) electron-energy-loss spectrometer. The latter system also has a LEED station and can be fitted with a UV resonance lamp. An add-on SIMS system is available for use with either chamber.

310 INSTRUMENTAL EFFECTS ON ESCA SPECTROSCOPIC INFORMATION, John S. Hammond and Thomas W. Rusch, Perkin-Elmer Corporation, Physical Electronics Division, 6509 Flying Cloud Drive, Eden Prairie, Minnesota 55344.

Electron Spectroscopy of Chemical Analysis (ESCA) or X-Ray Photoelectron Spectroscopy (XPS) has growing acceptance as a technique for both quantitative and chemical analyses of solid surfaces. Theoretical models and experimental results exist for the extraction of quantitative information from photoelectron signal intensities and chemical information from photoelectron and Auger electron kinetic energies.

Round robin analyses of equivalent samples on different instruments indicate that instrumental variations are of sufficient magnitude to be a limitation on the ability to fully extract information from ESCA spectra. These instrumental variations can be due to inherent properties of the samples (such as topographic or conductivity variations) or properties of the x-ray source, electron optics, detector, and their respective electronics.

The relationship of instrumental parameters to quantitative and chemical information will be discussed. For example, the stability and reproducibility of the photoelectron and Auger electron kinetic energy measurements to better than ±0.25eV allows the Auger parameters to be used for silicon and aluminum chemical state determination. The maintenance of constant analysis area as a function of analyzer retarding voltage allows the use of high and low kinetic energy photoelectron lines for non-destructive near-surface depth profile determination.

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311 ANALYSIS OF CORROSION PRODUCTS ON STAINLESS STEEL SURFACES: Correlative Use of Auger, SIMS and Radioactive Implant Studies* N. S. McIntyre, W. J. Chauvin, D. Johnston and F. E. Doern, Surface Science Western, The University of Western Ontario, P+A Bldg. 101, London, Ontario, Canada, N6A 3K7 and E. McAlpine and D. Lister, Chalk River Nuclear Laboratories, Chalk River, Ontario, Canada

In water-cooled nuclear reactors, corrosion products in the coolant stream account for an important fraction of the long-term radioactivity present in the boilers. It is therefore important to understand the mechanisms for release of each element into the coolant from typical boiler materials. As well, compositional information on the more passive oxide film which eventually forms on the alloy surface is being sought. This particular study has monitored the changes in film composition on a polished 304 stainless steel surface following its exposure in a circulating water loop at 290°C, for periods of 4 - 500 hours. In addition to Scanning Auger Microscopy (SAM) and Secondary Ion Mass Spectrometry (SIMS) studies of the surface films, complementary measurements of ionic redistribution during corrosion were made using radioactively "tagged" elements implanted into the alloy before its oxidation. The depth from which cations of cobalt chromium and iron migrate outward to the surface is found, from the tracer experiments, to be substantially smaller than the depth to which oxygen has penetrated the alloy, as measured by SAM. Thus, internal oxidation processes appear to be important even during the first 48 hours of corrosion. Both SAM and SIMS have been used to identify localized pockets of corrosion products which nucleate in surface scratches and which have a different composition than the general corrosion film.

*This work was supported by the Electric Power Research Institute

312 APPLICATIONS OF COMPLEMENTARY MICROPROBE ANALYSES TO PHOTOVOLTAIC DEVICES. L. L. Kazmerski, Solar Energy Research Institute, 1617 Cole Boulevard, Golden, Colorado 80401

Complementary microanalysis techniques (scanning AES, EELS, SIMS, XPS, EDS) are applied to photovoltaic devices in order to assess the surface and interface properties that limit solar cell performance. Results of these chemical and compositional studies are correlated directly with microelectrical measurements using EBIC and EBIV. Si and GaAs grain boundary chemistry and composition are investigated using scanning AES with better than 500 A spatial resolution. In-situ, ultrahigh vacuum fracturing is used to expose the intergrain regions for segregated impurity mapping. The electrical activity of various elemental species is evaluated. Oxygen segregation at high processing temperatures (>650°C) is shown to correlate with grain boundary electrical activity measured by EBIC. Metal-semiconductor and heterojunction interfaces are analyzed for the Cd(Zn)S/$CuInSe_2$ thin-film solar cell. Back contact interfacial chemistry is correlated with Schottky-barrier formation. The effects of heat-treatment in oxygen are related to heterojunction activation in these devices. Angular-resolved XPS and EELS are used to provide information on the Cd(Zn)S/Cu-ternary heterointerface chemistry. The limitations and positive features of the various microanalysis methods are emphasized.

313 COMPOSITIONAL INTEGRITY OF THE $CuInSe_2$ BILAYER IN A Cd(Zn)S/$CuInSi_2$ SOLAR CELL. Thomas P. Massopust, L. L. Kazmerski and Philip J. Ireland, Solar Energy Research Institute, PV Devices and Measurements Branch, 1617 Cole Boulevard, Golden, Colorado 80401

A thin-film photovoltaic solar cell is characterized chemically by using Scanning Auger Electron Microscopy (SAEM) and electrically, by charge collection methods (EBIC). Incorporation of the necessary hardware for EBIC into a scanning Auger instrument allows for microelectrical and microcompositional analysis of identical cross-sections of the cell. The techniques are applied specifically to the absorber region ($CuInSe_2$) of a Cd(Zn)S/$CuInSe_2$ device. The absorber (or collector) region of the cell is actually composed of two $CuInSe_2$ films; a low resistivity layer grown at 350°C and a high resistivity layer grown at 450°C with a 30% reduction in the Cu:In arrival rate. Variations in the elemental distribution would be expected from growth parameter changes of this magnitude. However, cross-sectional Auger line scans and depth profiles show uniformity of the Cu, In and Se throughout the Cu-ternary bilayer, within the 0.1 atomic % limit of detectability for Auger analysis. This is due to the redistribution of Cu during the 450°C growth period caused by the relatively high diffusion coefficient for Cu.

314 LEACHING PROPERTIES AND SURFACE STUDIES OF A GLASS PREPARED WITH RADIOACTIVE ZIRCONIA CALCINE, B. A. Staples, H. S. Cole, and D. A. Pavlica, Exxon Nuclear Idaho Company, Inc., P. O. Box 2800, Idaho Falls, Idaho 83401

Zirconia calcine, solidified high-level waste from the reprocessing of government and defense nuclear fuel, is the bulk of the wastes stored at the Idaho Chemical Processing Plant. Because of potential regulatory criteria, calcine may be judged unsuitable as a final waste form. For this reason, a glass has been developed to immobilize zirconia calcine by vitrification. It is the intent of this paper to present the analytical results of durability studies of glass prepared both from simulated and from actual radioactive calcine. Radioactive calcine glass contains fission products and actinides not present in the simulated calcine glass. To evaluate the stability of the glass under possible underground repository conditions, rates of release of ions into water from the glass were measured. Radioassay, ICP and flame AES were used to analyze leachate solutions and the leached glass to determine the fraction of total contained elements leached. ESCA, SIMS and SEM-XES were used for evaluation of the leached glass surface. The results demonstrate that the glass prepared with actual calcine is similar to glass prepared with simulated calcine and that minor amounts of actinides and fission products are leached.

315 LIGAND HYPERFINE SPECTRA OF Cu^{+2} IN AgCl. W. B. Paul, L. Rowan, L. Slifkin, Department of Physics and Astronomy, University of North Carolina, Chapel Hill, N.C. 27514. L. Rowan.

EPR studies of crystals of AgCl doped with Cu^{+2} show a rich hyperfine structure. The hyperfine structure is a sum of the hyperfine structure from the Cu nucleus and the super-hyperfine structure from the four Cl ligand nuclei in the plane perpendicular to the z-axis of the crystal. The super-hyperfine constants transferred to the Cu^{+2} ($3d^9$) hole, through the bonding with the Cl ions in the lattice, are approximately A = 20 G, and B = 3 G. The super-hyperfine constants are compared with other isoelectric paramagnetic ions in AgCl.

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